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(54) **Black iron-based composite particles, process for producing the same, paint and rubber or resin composition containing the same**

(57) Black iron-based composite particles of the present invention comprise:

- (i) black iron oxide particles or black iron oxide hydroxide particles having an average particle size of 0.08 to 1.0  $\mu\text{m}$ ;
- (ii) a coating layer formed on the surface of said particles (i) said coating layer comprising an organosilicon compound which is:

- (1) an organosilane compound obtainable by drying or heat-treating an alkoxysilane compound,
- (2) a polysiloxane or modified polysiloxane, or

(3) a fluoroalkyl organosilane compound obtainable by drying or heat-treating a fluoroalkylsilane compound; and

(iii) carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$ , adhered on at least a part of said coating layer. Such composite particles have excellent dispersibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the composite particles. They also have a high blackness substantially identical to a blackness of carbon black fine particles used alone, even when carbon black is contained therein only in a small amount.

EP 0 913 431 A2

## Description

[0001] The present invention relates to black iron-based composite particles, a process for producing the black iron-based composite particles, and a paint and a rubber or resin composition containing the black iron-based composite particles. More particularly, the present invention relates to black iron-based composite particles not only having an excellent dispersibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the black iron-based composite particles and a high blackness substantially identical to a blackness of carbon black fine particles used solely, even when carbon black is contained therein only in a small amount, but also capable of providing a paint for providing a coating film having an excellent acid resistance or a resin composition having an excellent aging resistance; a process for producing the black iron-based composite particles; a paint containing the black iron-based composite particles, which is excellent in acid resistance; and a rubber or resin composition containing the black iron-based composite particles, which is excellent in aging resistance.

[0002] Carbon black fine particles or magnetite particles are well known in the art as typical black pigments, and have been hitherto widely used as colorants for paints, printing ink, cosmetics, rubber or resin compositions or the like.

[0003] Among these black pigments, the carbon black fine particles are most excellent in blackness, and a coating film and rubber or resin composition prepared by using the carbon black fine particles also have an excellent acid resistance or aging resistance. However, since the carbon black fine particles have an average particle size as fine as about 0.005 to 0.05  $\mu\text{m}$ , it has been difficult to disperse the particles in a vehicle, or a rubber or resin composition. Further, since the carbon black fine particles have a bulk density as high as about 0.1  $\text{g}/\text{cm}^3$ , it has been difficult to handle the particles, resulting in deteriorated workability. Furthermore, it is also known that the carbon black fine particles have problems concerning safety and hygiene, such as carcinogenesis.

[0004] That is, as the amount of the carbon black fine particles used is increased, the blackness tends to become higher. However, when a larger amount of the carbon black fine particles is used, it is more and more difficult to disperse the particles in a vehicle, or a rubber or resin composition, resulting in not only deteriorated workability but also unfavorably causing problems concerning safety and hygiene.

[0005] On the other hand, the magnetite particles have a more appropriate particle size than that of the carbon black fine particles, especially an average particle size of about 0.08 to 1.0  $\mu\text{m}$  and are, therefore, excellent in dispersibility in a vehicle, or a rubber or resin composition, resulting in a high handling property. Further, the magnetite particles can show a further advantage such as non-toxicity. However, the magnetite particles are still unsatisfactory in blackness, and the coating film and the rubber or resin composition prepared by using the magnetite particles are also unsatisfactory in acid resistance and aging resistance.

[0006] Further, the magnetite particles tend to be magnetically aggregated because of magnetic attracting property thereof. In consequence, in order to improve the dispersibility in a vehicle, or a rubber or resin composition, it is known to use, as non-magnetic black iron-based particles, manganese-containing hematite particles or manganese-containing iron oxide hydroxide particles. However, the blackness of these particles is inferior to that of the magnetite particles.

[0007] In recent years, it has been required to improve various properties of black particles as colorants. There has been a strong demand for such black particles capable of showing useful properties of the carbon black fine particles as well as those of black iron oxide particles such as magnetite particles and black manganese-containing hematite particles or black iron oxide hydroxide particles such as black manganese-containing goethite particles.

[0008] Especially, it has been strongly demand to provide such black particles capable of showing a high blackness substantially identical to a blackness of the carbon black fine particles used solely, even when the carbon black fine particles which are deteriorated in workability such as handling property and have problems concerning safety and hygiene, are contained therein only in a small amount; capable of providing a paint for providing a coating film having an excellent acid resistance or a resin composition having an excellent aging resistance; and further capable of exhibiting an excellent dispersibility in a vehicle, or a rubber or resin composition.

[0009] To satisfy these demands, it has been attempted to produce black composite particles composed of the carbon black fine particles and the magnetite particles, and having useful properties of both the particles. For example, there are known 1) a method comprising steps of adding a water dispersion containing carbon black fine particles to a water suspension containing magnetite particles precipitated from an aqueous solution and then mixing and stirring the resultant mixture, thereby causing the carbon black fine particles to be absorbed onto surfaces of the magnetite particles (Japanese Patent Publication (KOKOKU) No. 50-13300(1975)); 2) a method comprising a step of introducing an iron-containing waste sludge in which high-molecular weight organic materials such as molasses are dissolved, and a carbon black-containing hot gas into a spray reactor at a temperature of 450 to 850°C, thereby producing magnetite particles from iron salts and simultaneously bonding the carbon black onto surfaces of the obtained magnetite particles using the molasses as a binding accelerator (Japanese Patent Application Laid-open (KOKAI) No. 49-48725(1974)); 3) a method comprising steps of suspending carbon black in an iron salt-containing aqueous solution and then adding alkali to the resultant suspension to coprecipitate carbon black and magnetite particles, thereby obtaining a co-precip-

itated product whose surfaces are coated with carbon black (Japanese Patent Publication (KOKOKU) No. 55-39580 (1980)); 4) a method comprising steps of adhering carbon black or the like on surfaces of fine plate-like particles and fixing the carbon black or the like thereon using an anionic or cationic surfactant, a nonionic surfactant and an organic functional silane compound (Japanese Patent Application Laid-open (KOKAI) Nos. 6-145556(1994) and 7-316458 (1995)); or the like.

[0010] At present, it has been most demanded to provide black particles having useful properties of the carbon black fine particles as well as those of the black iron oxide particles or black iron oxide hydroxide particles. However, all of the above mentioned known methods have failed to provide black particles satisfying these useful properties. Specifically, in the case of the above-mentioned method 1), the desorption percentage of the carbon black fine particles still remains high as described in Comparative Examples hereinafter. As a result, when the carbon black-adsorbed magnetite particles are dispersed in vehicle or resin compositions, the carbon black fine particles are desorbed therefrom, i.e., it becomes difficult to uniformly disperse the black particles in vehicles and resin compositions, thereby failing to sufficiently improve the blackness of a paint and rubber or resin composition prepared therefrom.

[0011] In the case of the above-mentioned method 2), in order to obtain black particles having a high blackness substantially identical to a blackness of carbon black fine particles used solely, it is required to use the carbon black fine particles in an amount as large as about 250 parts by weight based on 100 parts by weight of the magnetite particles. In the case of the above-mentioned method 3), in order to obtain black particles having a high blackness substantially identical to a blackness of carbon black fine particles used solely, it is also required to use the carbon black fine particles in an amount as large as about 100 to 400 parts by weight based on 100 parts by weight of the magnetite particles. In addition, the carbon black fine particles tend to be desorbed from the surfaces of the co-precipitated product. Further, in the case of the above-mentioned method 4), the particles obtained by this method are not only deteriorated in blackness, but also show a high percentage of desorption of the carbon black fine particles therefrom. Besides, such particles obtained by the method 4) are not black particles.

[0012] As a result of the present inventors' earnest studies, it has been found that by forming a coating layer composed of at least one organosilicon compound selected from the group consisting of (1) organosilane compounds obtained by drying or heat-treating alkoxysilane compounds, (2) polysiloxanes or modified polysiloxanes and (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating fluoroalkylsilane compounds, on surface of specific black iron oxide particle or black iron oxide hydroxide particle, and adhering carbon black fine particles on the coating layer such that the amount of the carbon black fine particles adhered is 1 to 30 parts by weight based on 100 parts by weight of the black iron oxide particles or black iron oxide hydroxide particles, the obtained black iron-based composite particles can have an excellent dispersibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the black iron-based composite particles and a high blackness substantially identical to a blackness of carbon black fine particles used solely, even when the carbon black is contained therein only in a small amount, and can provide a coating film having an excellent acid resistance and a rubber or resin composition having an excellent aging resistance. The present invention has been attained on the basis of the above finding.

[0013] An object of the present invention is to provide black iron-based composite particles not only having a high blackness substantially identical to a blackness of carbon black fine particles used solely, even when carbon black is contained therein only in a small amount, but also capable of providing a paint for providing a coating film having an excellent acid resistance and a rubber or resin composition having an excellent aging resistance.

[0014] Another object of the present invention is to provide black iron-based composite particles showing a low percentage of desorption of carbon black therefrom, and an excellent dispersibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the black iron-based composite particles.

[0015] A further object of the present invention is to provide a process for producing black iron-based composite particles not only having an excellent dispersibility in a vehicle, or a rubber or resin composition and showing a high blackness substantially identical to a blackness of carbon black fine particles used solely, even when carbon black is contained therein only in a small amount, but also capable of providing a paint for providing a coating film having an excellent acid resistance and a rubber or resin composition having an excellent aging resistance.

[0016] A still further object of the present invention is to provide a paint showing less change in gloss and lightness according to an acid resistance test for coating films.

[0017] A still further object of the present invention is to provide a rubber or resin composition which exhibits a small deterioration of the rubber or resin used therein.

[0018] To accomplish the aims, in a first aspect of the present invention, there is provided black iron-based composite particles comprising:

as a core particle black iron oxide particle or black iron oxide hydroxide particle having an average particle size of 0.08 to 1.0  $\mu\text{m}$ ;

a coating layer formed on surface of the black iron oxide particle or black iron oxide hydroxide particle, comprising at least one organosilicon compound selected from the group consisting of (1) organosilane compounds obtained by drying or heat-treating alkoxysilane compounds, (2) polysiloxanes, or modified polysiloxanes and (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating fluoroalkylsilane compounds; and

carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$ , adhered (attached) onto the coating layer,

the amount of the carbon black fine particles adhered being 1 to 30 parts by weight based on 100 parts by weight of the black iron oxide particles or black iron oxide hydroxide particles.

[0019] In a second aspect of the present invention, there is provided black iron-based composite particles comprising:

black iron oxide particles or black iron oxide hydroxide particles having an average particle size of 0.08 to 1.0  $\mu\text{m}$ ;

an underlayer formed on surface of the black iron oxide particle or black iron oxide hydroxide particle, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon;

a coating layer formed on the surface of the underlayer, comprising at least one organosilicon compound selected from the group consisting of (1) organosilane compounds obtained by drying or heat-treating alkoxysilane compounds, (2) polysiloxanes, or modified polysiloxanes and (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating fluoroalkylsilane compounds; and

carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$ , adhered (attached) onto the coating layer,

the amount of the carbon black fine particles adhered being 1 to 30 parts by weight based on 100 parts by weight of the black iron oxide particles or black iron oxide hydroxide particles.

[0020] In a third aspect of the present invention, there is provided a process for producing black iron-based composite particles defined in the first aspect, which process comprises:

mixing and stirring said black iron oxide particles or black iron oxide hydroxide particles having an average particle size of 0.08 to 1.0  $\mu\text{m}$  together with at least one compound selected from the group consisting of:

- (1) alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkylsilane compounds

by using an edge runner, thereby coating surfaces of said black iron oxide particles or black iron oxide hydroxide particles with said compounds;

adding carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$  in an amount of 1 to 30 parts by weight based on 100 parts by weight of said black iron oxide particles or black iron oxide hydroxide particles, thereby obtaining mixed particles;

mixing and stirring said mixed particles by using an edge runner, followed by drying or heat-treating, thereby adhering said carbon black fine particles on the surface of a coating layer comprising the organosilicon compounds;

[0021] In a fourth aspect of the present invention, there is provided a paint comprising:

said black iron-based composite particles defined in the first aspect or second aspect; and  
a paint base material.

[0022] In a fifth aspect of the present invention, there is provided a rubber or resin composition comprising:

said black iron-based composite particles defined in the first aspect or second aspect; and  
a base material for rubber or resin composition.

In the accompanying drawings:

[0023]

Fig. 1 is an electron photograph (x 20,000) showing a particle structure of black manganese-containing hematite particles used in Example 1:

Fig. 2 is an electron photograph (x 20.000) showing a particle structure of carbon black fine particles used in Example 1;

Fig. 3 is an electron photograph (x 20.000) showing a particle structure of black iron-based composite particles obtained in Example 1; and

Fig. 4 is an electron photograph (x 20.000) showing a particle structure of mixed particles of black manganese-containing hematite particles and carbon black fine particles for comparative purposes.

[0024] The particle shape and particle size of the black iron-based composite particles according to the present invention are considerably varied depending upon those of black iron oxide particles or black iron oxide hydroxide particles as core particles. Specifically, the black iron-based composite particles according to the present invention are substantially similar in particle shape to that of the core particles, and have a slightly larger particle size than that of the core particles.

[0025] The black iron-based composite particles according to the present invention may have such a particle size as defined below:

(i) In the case where the core particles are granular particles, the lower limit of the average particle size of the black iron-based composite particles is usually  $0.082\text{ }\mu\text{m}$ , preferably  $0.1\text{ }\mu\text{m}$ , and the upper limit thereof is usually  $1.05\text{ }\mu\text{m}$ , preferably  $0.7\text{ }\mu\text{m}$ , more preferably  $0.5\text{ }\mu\text{m}$ .

(ii) In the case where the core particles are acicular or spindle-shaped particles, the lower limit of the average particle size (average major axis diameter) of the black iron-based composite particles is usually  $0.082\text{ }\mu\text{m}$ , preferably  $0.1\text{ }\mu\text{m}$  and the upper limit thereof is usually  $1.05\text{ }\mu\text{m}$ , preferably  $0.7\text{ }\mu\text{m}$ , more preferably  $0.5\text{ }\mu\text{m}$ ; and the lower limit of the aspect ratio (average major axis diameter/average minor axis diameter) of the black iron-based composite particles is usually 2, preferably 3, and the upper limit thereof is usually 20, preferably 15, more preferably 10.

(iii) In the case where the core particles are plate-like particles, the lower limit of the average particle size (average plate surface diameter) of the black iron-based composite particles is usually  $0.082\text{ }\mu\text{m}$ , preferably  $0.1\text{ }\mu\text{m}$ , and the upper limit thereof is usually  $1.05\text{ }\mu\text{m}$ , preferably  $0.7\text{ }\mu\text{m}$ , more preferably  $0.5\text{ }\mu\text{m}$ ; and the lower limit of the plate ratio (average plate surface diameter/average thickness) of the black iron-based composite particles is usually 2, preferably 3, and the upper limit thereof is usually 50, preferably 20, more preferably 10.

[0026] When the average particle size of the black iron-based composite particles is less than  $0.082\text{ }\mu\text{m}$ , the intermolecular force between the particles may be increased due to the fineness thereof, so that it may become difficult to uniformly disperse the particles in a vehicle, or a rubber or resin composition. On the other hand, when the average particle size is more than  $1.05\text{ }\mu\text{m}$ , it may become difficult to uniformly disperse the particles in a vehicle, or a rubber or resin composition due to the largeness thereof.

[0027] The upper limit of the blackness of the black iron-based composite particles according to the present invention is preferably 18 when represented by a  $L^*$  value thereof. When the  $L^*$  value as the upper limit of the blackness is more than 18, the lightness of the black iron-based composite particles is increased and, therefore, the blackness thereof may become insufficient. The upper limit of the blackness is more preferably 17.8 when represented by a  $L^*$  value. The lower limit of the blackness is preferably about 15 when represented by a  $L^*$  value.

[0028] The percentage of desorption of carbon black fine particles from the black iron-based composite particles according to the present invention is usually not more than 20 %, preferably not more than 10 %. When the desorption percentage of carbon black fine particles is more than 20 %, the desorbed carbon black fine particles tend to inhibit the composite particles from being uniformly dispersed in a vehicle, or a rubber or resin composition upon the production of a paint or a rubber or resin composition.

[0029] The black iron-based composite particles according to the present invention have a BET specific surface area of usually  $1.0$  to  $200\text{ m}^2/\text{g}$ , preferably  $2.0$  to  $150\text{ m}^2/\text{g}$ , more preferably  $2.5$  to  $100\text{ m}^2/\text{g}$ .

[0030] When the BET specific surface area of the black iron-based composite particles according to the present invention is less than  $1.0\text{ m}^2/\text{g}$ , coarse particles may be produced or sintered particles may be formed therein or therebetween, resulting in adversely affecting the dispersibility of the particles in a vehicle, or a rubber or resin composition. On the other hand, when the BET specific surface area is more than  $200\text{ m}^2/\text{g}$ , the intermolecular force between the particles is increased due to the fineness thereof, so that it may become difficult to disperse the particles in a vehicle, or a rubber or resin composition.

[0031] Further, it is preferred that the black iron-based composite particles according to the present invention have a geometrical standard deviation of particle sizes of not more than 1.80. When the geometrical standard deviation of particle sizes is more than 1.80, coarse particles tend to be present in the composite particles, so that it may become difficult to uniformly disperse the particles in a vehicle or a rubber or resin composition. In view of uniform dispersion of the black iron-based composite particles in a vehicle, or a rubber or resin composition, the geometrical standard

deviation of particle sizes of the black iron-based composite particles according to the present invention is preferably not more than 1.70. Further, in view of industrial production of the black iron-based composite particles, the lower limit of the geometrical standard deviation of particle sizes is preferably 1.01.

[0032] As the black iron oxide particles used as the core particles of the black iron-based composite particles according to the present invention, there may be exemplified magnetite particles or manganese-containing hematite particles which contain manganese in an amount of 5 to 40 % by weight based on the weight of the manganese-containing hematite particles. As the black iron oxide hydroxide particles used as the core particles of the black iron-based composite particles according to the present invention, there may be exemplified manganese-containing goethite particles which contain manganese in an amount of 5 to 40 % by weight based on the weight of the manganese-containing goethite particles.

[0033] Meanwhile, the particle shape of the black iron oxide particles or the black iron oxide hydroxide particles as the core particles is not particularly restricted. For example, there may be used such black iron oxide particles or black iron oxide hydroxide particles having a spherical shape, an octahedral shape, a hexahedral shape, a polyhedral shape, a granular shape, an acicular shape, a spindle-like shape, a plate-like shape or the like.

[0034] The black iron oxide particles or the black iron oxide hydroxide particles as the core particles may have such a particle size as defined below.

(i) In the case where the core particles have a spherical shape, an octahedral shape, a hexahedral shape, a polyhedral shape or a granular shape, the lower limit of the average particle size of the core particles is usually 0.08  $\mu\text{m}$ , preferably 0.098  $\mu\text{m}$ , and the upper limit thereof is usually 1.0  $\mu\text{m}$ , preferably 0.68  $\mu\text{m}$ , more preferably 0.48  $\mu\text{m}$ .

(ii) In the case where the core particles are acicular particles or spindle-shaped particles, the lower limit of the average particle size (average major axis diameter) of the core particles is usually 0.08  $\mu\text{m}$ , preferably 0.098  $\mu\text{m}$ , and the upper limit thereof is usually 1.0  $\mu\text{m}$ , preferably 0.68  $\mu\text{m}$ , more preferably 0.48  $\mu\text{m}$ ; and the lower limit of the aspect ratio (average major axis diameter/average minor axis diameter) of the core particles is usually 2, preferably 3, and the upper limit thereof is usually 20, preferably 15, more preferably 10.

(iii) In the case where the core particles are plate-like particles, the lower limit of the average particle size (average plate surface diameter) of the core particles is usually 0.08  $\mu\text{m}$ , preferably 0.098  $\mu\text{m}$ , and the upper limit thereof is usually 1.0  $\mu\text{m}$ , preferably 0.68  $\mu\text{m}$ , more preferably 0.48  $\mu\text{m}$ ; and the lower limit of the plate ratio (average plate surface diameter/average thickness) of the core particles is usually 2, preferably 3, and the upper limit thereof is usually 50, preferably 20, more preferably 10.

[0035] With respect of the blackness of the black iron oxide particles as the core particles, in case of the magnetic particles, the lower limit of the blackness thereof, when represented by the  $L^*$  value, is usually 18, and the upper limit thereof is usually 25, preferably 24. In the case of the black manganese-containing hematite particles, the lower limit of the blackness thereof as the core particles when represented by the  $L^*$  value, is usually 18, and the upper limit thereof is usually 30, preferably 28, more preferably 25.

[0036] With respect to the blackness of the black iron oxide hydroxide particles as the core particles, in the case of the manganese-containing goethite particles, the lower limit of the blackness thereof, when represented by the  $L^*$  value, is usually 18, and the upper limit thereof is usually 30, preferably 28, more preferably 25.

[0037] When the  $L^*$  value is more than the above upper limit, the blackness of the core particles is insufficient, thereby failing to obtain the black iron-based composite particles having an excellent blackness according to the present invention.

[0038] The black iron oxide particles or black iron oxide hydroxide particles as the core particles may have a BET specific surface area of usually 1.0 to 200  $\text{m}^2/\text{g}$ , preferably 2.0 to 150  $\text{m}^2/\text{g}$ , more preferably 2.5 to 100  $\text{m}^2/\text{g}$ .

[0039] Further, it is preferred that the black iron oxide particles or the black iron oxide hydroxide particles used as the core particles in the present invention have a geometrical standard deviation of particle sizes of not more than 1.8, preferably not more than 1.7. The lower limit of the geometrical standard deviation of particle sizes of the core particles is preferably 1.01.

[0040] The coating layer formed on the surfaces of the core particles comprises at least one organosilicon compound selected from the group consisting of (1) organosilane compounds obtained by drying or heat-treating alkoxysilane compounds; (2) polysiloxanes, or modified polysiloxanes selected from the group consisting of (A) polysiloxanes modified with at least one compound selected from the group consisting of polyethers, polyesters and epoxy compounds (hereinafter referred to merely as "modified polysiloxanes"), and (B) polysiloxanes whose molecular terminal is modified with at least one group selected from the group consisting of carboxylic acid groups, alcohol groups and a hydroxyl group; and (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating fluoroalkylsilane compounds.

[0041] The organosilane compounds (1) can be produced by drying or heat-treating alkoxysilane compounds represented by the formula (I):

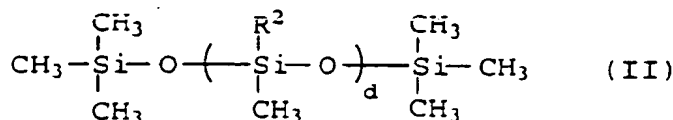


wherein  $R^1$  is  $C_6H_5-$ ,  $(CH_3)_2CHCH_2-$  or  $n-C_mH_{2m+1}-$  (wherein  $b$  is an integer of 1 to 18);  $X$  is  $CH_3O-$  or  $C_2H_5O-$ ; and  $a$  is an integer of 0 to 3.

[0042] The drying or heat-treatment of the alkoxysilane compounds is conducted, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours.

[0043] Specific examples of the alkoxysilane compounds may include methyl triethoxysilane, dimethyl diethoxysilane, tetraethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane, tetramethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, isobutyl trimethoxysilane, decyl trimethoxysilane or the like. Among these alkoxysilane compounds, in view of the desorption percentage and the adhering effect of carbon black fine particles, methyl triethoxysilane, phenyl triethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane and isobutyl trimethoxysilane are preferred, and methyl triethoxysilane and methyl trimethoxysilane are more preferred.

[0044] As the polysiloxanes (2), there may be used those compounds represented by the formula (II):

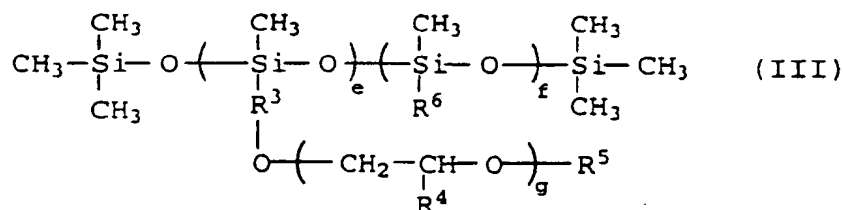


wherein  $R^2$  is  $H-$  or  $CH_3-$ , and  $d$  is an integer of 15 to 450.

[0045] Among these polysiloxanes, in view of the desorption percentage and the adhering effect of carbon black fine particles, polysiloxanes having methyl hydrogen siloxane units are preferred.

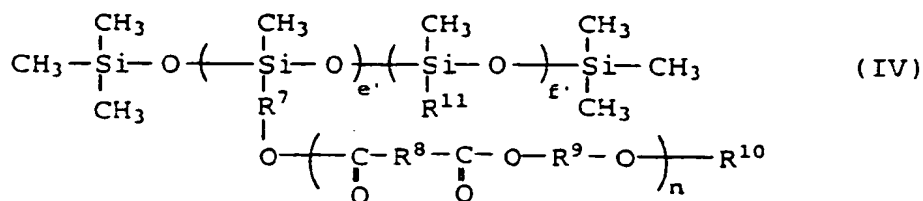
[0046] As the modified polysiloxanes (A), there may be used:

(a) polysiloxanes modified with polyethers represented by the formula (III):



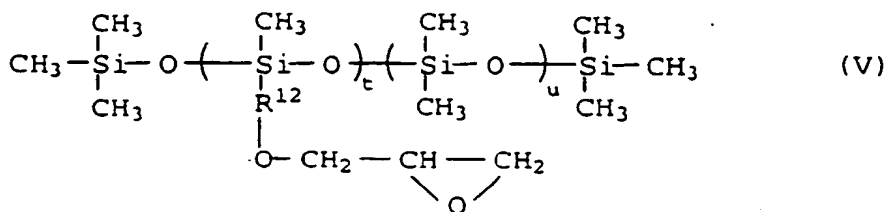
wherein  $R^3$  is  $-(-CH_2-)_h-$ ;  $R^4$  is  $-(-CH_2-)_i-CH_3$ ;  $R^5$  is  $-OH$ ,  $-COOH$ ,  $-CH=CH_2$ ,  $-CH(CH_3)=CH_2$  or  $-(-CH_2-)_j-CH_3$ ;  $R^6$  is  $-(-CH_2-)_k-CH_3$ ;  $g$  and  $h$  are an integer of 1 to 15;  $i$ ,  $j$  and  $k$  are an integer of 0 to 15;  $e$  is an integer of 1 to 50; and  $f$  is an integer of 1 to 300;

(b) polysiloxanes modified with polyesters represented by the formula (IV):



wherein  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  are  $-(\text{CH}_2)_q-$  and may be the same or different;  $\text{R}^{10}$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}(\text{CH}_3)=\text{CH}_2$  or  $-(\text{CH}_2)_r-\text{CH}_3$ ;  $\text{R}^{11}$  is  $-(\text{CH}_2)_s-\text{CH}_3$ ;  $n$  and  $q$  are an integer of 1 to 15;  $r$  and  $s$  are an integer of 0 to 15;  $e'$  is an integer of 1 to 50; and  $f'$  is an integer of 1 to 300;

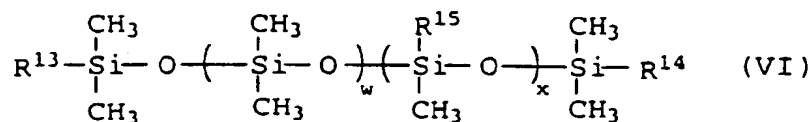
(c) polysiloxanes modified with epoxy compounds represented by the formula (V):



wherein  $\text{R}^{12}$  is  $-(\text{CH}_2)_v-$ ;  $v$  is an integer of 1 to 15;  $t$  is an integer of 1 to 50; and  $u$  is an integer of 1 to 300; or a mixture thereof.

[0047] Among these modified polysiloxanes (A), in view of the desorption percentage and the adhering effect of carbon black fine particles, the polysiloxanes modified with the polyethers represented by the formula (III), are preferred.

[0048] As the terminal-modified polysiloxanes (B), there may be used those represented by the formula (VI):



wherein  $\text{R}^{13}$  and  $\text{R}^{14}$  are  $-\text{OH}$ ,  $\text{R}^{16}\text{OH}$  or  $\text{R}^{17}\text{COOH}$  and may be the same or different;  $\text{R}^{15}$  is  $-\text{CH}_3$  or  $-\text{C}_6\text{H}_5$ ;  $\text{R}^{16}$  and  $\text{R}^{17}$  are  $-(\text{CH}_2)_y-$ ;  $y$  is an integer of 1 to 15;  $w$  is an integer of 1 to 200; and  $x$  is an integer of 0 to 100.

[0049] Among these terminal-modified polysiloxanes, in view of the desorption percentage and the adhering effect of carbon black fine particles, the polysiloxanes whose terminals are modified with carboxylic acid groups are preferred.

[0050] The fluoroalkyl organosilane compounds (3) may be produced by drying or heat-treating fluoroalkylsilane compounds represented by the formula (VII):



wherein  $\text{R}^{13}$  is  $\text{CH}_3-$ ,  $\text{C}_2\text{H}_5-$ ,  $\text{CH}_3\text{O}-$  or  $\text{C}_2\text{H}_5\text{O}-$ ;  $\text{X}$  is  $\text{CH}_3\text{O}-$  or  $\text{C}_2\text{H}_5\text{O}-$ ; and  $z$  is an integer of 0 to 15; and  $a'$  is an integer of 0 to 3.

[0051] The drying or the heat-treatment of the fluoroalkylsilane compounds may be conducted, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours.



[0052] Specific examples of the fluoroalkylsilane compounds may include trifluoropropyl trimethoxysilane, tridecafluorooctyl trimethoxysilane, heptadecafluorodecyl trimethoxysilane, heptadecafluorodecylmethyl dimethoxysilane, trifluoropropyl triethoxysilane, tridecafluorooctyl triethoxysilane, heptadecafluorodecyl triethoxysilane, heptadecafluorodecylmethyl diethoxysilane or the like. Among these fluoroalkylsilane compounds, in view of the desorption percentage and the adhering effect of carbon black fine particles, trifluoropropyl trimethoxysilane, tridecafluorooctyl trimethoxysilane and heptadecafluorodecyl trimethoxysilane are preferred, and trifluoropropyl trimethoxysilane and tridecafluorooctyl trimethoxysilane are more preferred.

[0053] The coating amount of the organosilicon compounds is usually 0.02 to 5.0 % by weight, preferably 0.03 to 2.0 % by weight, more preferably 0.05 to 1.5 % by weight (calculated as Si) based on the weight of the black iron oxide particles or the black iron oxide hydroxide particles coated with the organosilicon compounds.

[0054] When the coating amount of the organosilicon compounds is less than 0.02 % by weight, it may become difficult to adhere carbon black fine particles on the coating layer in such an amount enough to improve the blackness thereof. On the other hand, even when the coating amount of the organosilicon compounds is more than 5.0 % by weight, a sufficient amount of carbon black fine particles can be adhered on the coating layer. However, it is meaningless because the blackness cannot be further improved by using such an excess amount of the organosilicon compounds.

[0055] As the carbon black fine particles used in the black iron-based composite particles according to the present invention, there may be exemplified commercially available carbon blacks such as furnace black or channel black. Specific examples of the commercially available carbon blacks usable in the present invention, may include MA-100, MA7, #1000, #2400B, #30, MA8, MA11, #50, #52, #45, #2200B, MA600, etc. (tradename, produced by MITSUBISHI CHEMICAL CORP.), SEAST 9H, SEAST 7H, SEAST 6, SEAST 3H, SEAST 300, SEAST FM, etc. (tradename, produced by TOKAI CARBON CO., LTD.) or the like. In view of the compatibility with the organosilicon compounds, MA-100, MA7, #1000, #2400B and #30 are preferred.

[0056] The average particle size of the carbon black fine particles is usually 0.005 to 0.05  $\mu\text{m}$ , preferably 0.010 to 0.035  $\mu\text{m}$ . When the average particle size of the carbon black fine particles is less than 0.005  $\mu\text{m}$ , the carbon black fine particles are too fine to be well handled. On the other hand, when the average particle size is more than 0.05  $\mu\text{m}$ , the particle size of the carbon black fine particles may become much larger than that of the black iron oxide particles or the black iron oxide hydroxide particles as the core particles, thereby causing insufficient adhesion of the carbon black fine particles onto the coating layer composed of the organosilicon compounds and increasing the desorption percentage of the carbon black fine particles. As a result, the dispersibility of the obtained composite particles in a vehicle, or a rubber or resin composition is deteriorated.

[0057] The ratio value of an average particle size of the black iron oxide particles or the black iron oxide hydroxide particles to an average particle size of the carbon black fine particles is preferably not less than 2. When the ratio value is less than 2, the particle size of the carbon black fine particles may become considerably large as compared to that of the black iron oxide particles or the black iron oxide hydroxide particles as the core particles, thereby causing insufficient adhesion of the carbon black fine particles onto the coating layer composed of the organosilicon compounds and increasing the desorption percentage of the carbon black fine particles. As a result, the dispersibility of the obtained composite particles in a vehicle, or a rubber or resin composition is deteriorated. The upper limit of the ratio value thereof is preferably 200.

[0058] The amount of the carbon black fine particles adhered is 1 to 30 parts by weight based on 100 parts by weight of the black iron oxide particles or the black iron oxide hydroxide particles as the core particles. When the amount of the carbon black fine particles adhered is less than 1 part by weight, the blackness of the resultant composite particles is unsatisfactory because of insufficient amount of the carbon black fine particles adhered onto the coating layer. On the other hand, when the amount of the carbon black fine particles adhered is more than 30 parts by weight, the carbon black fine particles tend to be desorbed from the coating layer because of too much amount of the carbon black fine particles adhered thereonto, though the obtained composite particles can show a sufficient blackness. As a result, the dispersibility of the obtained composite particles in a vehicle, or a rubber or resin composition is deteriorated.

[0059] In the black iron-based composite particles according to the present invention, the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles as the core particles may be preliminarily coated with at least one compound selected from the group consisting of hydroxide of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon (hereinafter referred to as "underlayer composed of hydroxides or oxides of aluminum or silicon"), if required. In this case, the dispersibility of the obtained composite particles in a vehicle, or a rubber or resin composition may become improved as compared to those having no underlayer composed of hydroxides or oxides of aluminum or silicon.

[0060] The coating amount of the hydroxides or oxides of aluminum or silicon is 0.01 to 50 % by weight calculated as Al,  $\text{SiO}_2$  or a sum of Al and  $\text{SiO}_2$ , based on the weight of the black iron oxide particles or the black iron oxide hydroxide particles as the core particles. When the coating amount of the hydroxides or oxides of aluminum or silicon is less than 0.01 % by weight, the dispersibility of the obtained composite particles in a vehicle, or a rubber or resin composition cannot be improved. On the other hand, when the coating amount of the hydroxides or oxides of aluminum

or silicon is more than 50 % by weight, the obtained composite particles can exhibit a good dispersibility in a vehicle, or a rubber or resin composition, but it is meaningless because the dispersibility cannot be further improved by using such an excess coating amount of the hydroxides or oxides of aluminum or silicon.

[0061] The black iron-based composite particles having the underlayer composed of the hydroxides or oxides of aluminum or silicon may be substantially identical in a particle size, a geometrical standard deviation of particle sizes, a BET specific surface area and a blackness ( $L^*$  value), to those having no underlayer composed of the hydroxides or oxides of aluminum or silicon.

[0062] Next, the process for producing the black iron-based composite particles according to the present invention, is described.

[0063] The granular magnetite particles as the core particles according to the present invention may be produced by a so-called wet process, i.e., by passing an oxygen-containing gas such as air through a suspension containing a ferrous hydroxide colloid obtained by reacting a ferrous salt aqueous solution with alkali hydroxide.

[0064] The acicular magnetite particles or the spindle-shaped magnetite particles may be produced by first forming acicular goethite particles or spindle-shaped goethite particles by a so-called wet process, i.e., by passing an oxygen-containing gas such as air through a suspension containing either ferrous hydroxide colloid, iron carbonate or iron-containing precipitates obtained by reacting a ferrous salt aqueous solution with alkali hydroxide, alkali carbonate or both of alkali hydroxide and alkali carbonate, and then after filtering-out and washing with water, heat-treating the resultant goethite particles at a temperature of 300 to 500°C in a reducing atmosphere.

[0065] The granular manganese-containing hematite particles as the core particles according to the present invention, may be produced by first forming coated magnetite particles by coating the granular magnetite particles obtained by the above-mentioned wet process, with a manganese compound such that the coating amount of manganese is 8 to 150 atomic % based on whole Fe, or forming magnetite particles containing manganese in an amount of 8 to 150 atomic % based on whole Fe by conducting the above-mentioned wet process for producing the granular magnetite particles in the presence of manganese, and then after filtering-out, washing with water and drying, heat-treating the resultant manganese-coated magnetite particles or the manganese-containing magnetite particles at a temperature of 750 to 1,000°C in an oxygen-containing gas such as air.

[0066] The manganese-containing hematite particles are non-magnetic material and, therefore, free from magnetic aggregation, thereby exhibiting a good dispersibility.

[0067] The acicular or spindle-shaped manganese-containing hematite particles may be produced by heat-treating acicular or spindle-shaped goethite particles containing manganese in an amount of 8 to 150 atomic % based on whole Fe which are obtained by the below-mentioned method, at a temperature of 400 to 800°C in an oxygen-containing gas such as air.

[0068] The acicular or spindle-shaped manganese-containing goethite particles according to the present invention, may be produced by conducting the above-mentioned wet process for producing the acicular or spindle-shaped goethite particles, in the presence of manganese, thereby forming acicular or spindle-shaped goethite particles containing manganese in an amount of 8 to 150 atomic % based on whole Fe.

[0069] The coating of the black iron oxide particles or the black iron oxide hydroxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds, may be conducted by mechanically mixing and stirring the black iron oxide particles or the black iron oxide hydroxide particles together with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds; or by mechanically mixing and stirring both the components together while spraying the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds onto the black iron oxide particles or the black iron oxide hydroxide particles. In these cases, substantially whole amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds added can be applied onto the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles.

[0070] In order to uniformly coat the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds, it is preferred that the black iron oxide particles or the black iron oxide hydroxide particles are preliminarily diaggregated by using a pulverizer. As the apparatuses for the mixing and stirring, there may be used an edge runner, a Henschel mixer or the like.

[0071] The conditions for the mixing and stirring such as mixing ratio, linear load or mixing and stirring time, may be appropriately adjusted so as to coat the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds as uniformly as possible. The mixing and stirring time for the coating treatment is, for example, preferably not less than 20 minutes.

[0072] The amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds added, is preferably 0.15 to 45 parts by weight based on 100

parts by weight of the black iron oxide particles or the black iron oxide hydroxide particles. When the amount of the organosilicon compounds added is less than 0.15 part by weight, it may become difficult to adhere the carbon black fine particles in such an amount enough to improve the blackness of the obtained composite particles. On the other hand, when the amount of the organosilicon compounds added is more than 45 parts by weight, a sufficient amount of the carbon black fine particles can be adhered on the surface of the coating layer, but it is meaningless because the blackness of the composite particles cannot be further improved by using such an excess amount of the organosilicon compounds.

**[0073]** Next, the carbon black fine particles are added to the black iron oxide particles or the black iron oxide hydroxide particles coated with the organosilicon compounds, and the resultant mixture is continuously mixed and stirred to adhere the carbon black fine particles on the surfaces of the coating layer composed of the organosilicon compounds, and then dried.

**[0074]** In the case where the alkoxysilane compounds (1) and the fluoroalkylsilane compounds (3) are used as the coating compound, after the carbon black fine particles are adhered on the surface of the coating layer, the resultant composite particles are dried or heat-treated, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours, thereby forming a coating layer composed of the organosilicon compounds (1) and the fluoroalkyl organosilicon compounds (3), respectively.

**[0075]** It is preferred that the carbon black fine particles are added little by little and slowly, especially about 5 to 60 minutes.

**[0076]** The conditions for mixing and stirring the black iron oxide particles or the black iron oxide hydroxide particles and the carbon black fine particles, such as mixing ratio, linear load or mixing and stirring time, may be appropriately adjusted so as to uniformly adhere the carbon black fine particles on the surface of the coating layer. The mixing and stirring time for the adhesion treatment is, for example, preferably not less than 20 minutes.

**[0077]** The amount of the carbon black fine particles added, is preferably 1 to 30 parts by weight based on 100 parts by weight of the black iron oxide particles or the black iron oxide hydroxide particles. When the amount of the carbon black fine particles added is less than 1 part by weight, it may become difficult to adhere the carbon black fine particles in such an amount enough to improve the blackness of the obtained composite particles. On the other hand, when the amount of the carbon black fine particles added is more than 30 parts by weight, a sufficient blackness of the resultant composite particles can be obtained, but the carbon black fine particles tend to be desorbed from the surface of the coating layer because of too large amount of the carbon black fine particles adhered, resulting in deteriorated dispersibility in a vehicle, or a rubber or resin composition.

**[0078]** The black iron oxide particles or the black iron oxide hydroxide particles may be coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon, if required, prior to mixing and stirring with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds.

**[0079]** The coating of the hydroxides or oxides of aluminum or silicon may be conducted by adding an aluminum compound, a silicon compound or both the compounds to a water suspension in which the black iron oxide particles or the black iron oxide hydroxide particles are dispersed, followed by mixing and stirring, and further adjusting the pH of the suspension, if required, thereby coating the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon. The thus obtained particles coated with the hydroxides or oxides of aluminum or silicon are then filtered out, washed with water, dried and pulverized. Further, the particles coated with the hydroxides or oxides of aluminum or silicon may be subjected to post-treatments such as deaeration treatment and compaction treatment.

**[0080]** As the aluminum compounds, there may be exemplified aluminum salts such as aluminum acetate, aluminum sulfate, aluminum chloride or aluminum nitrate, alkali aluminates such as sodium aluminate, alumina sols or the like.

**[0081]** The amount of the aluminum compound added is 0.01 to 50.00 % by weight (calculated as Al) based on the weight of the black iron oxide particles or the black iron oxide hydroxide particles. When the amount of the aluminum compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles with hydroxides or oxides of aluminum or silicon, thereby failing to improve the dispersibility in a vehicle, or a rubber or resin composition. On the other hand, when the amount of the aluminum compound added is more than 50.00 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the aluminum compound.

**[0082]** As the silicon compounds, there may be exemplified water glass #3, sodium orthosilicate, sodium metasilicate, colloidal silica or the like.

**[0083]** The amount of the silicon compound added is 0.01 to 50.00 % by weight (calculated as SiO<sub>2</sub>) based on the weight of the black iron oxide particles or the black iron oxide hydroxide particles. When the amount of the silicon compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles with hydroxides or oxides of silicon, thereby failing to improve

the dispersibility in a vehicle, or a rubber or resin composition. On the other hand, when the amount of the silicon compound added is more than 50.00 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the silicon compound.

[0084] In the case where both the aluminum and silicon compounds are used in combination for the coating, the total amount of the aluminum and silicon compounds added is preferably 0.01 to 50.00 % by weight (calculated as a sum of Al and SiO<sub>2</sub>) based on the weight of the black iron oxide particles or the black iron oxide hydroxide particles.

[0085] Next, the paint containing the black iron-based composite particles according to the present invention is described.

[0086] The solvent-based paint containing the black iron-based composite particles according to the present invention can exhibit a L\* value of 15 to 19.5 when formed into a coating film and, therefore, the blackness of the paint is substantially identical to the blackness of the carbon black fine particles solely, even when carbon black is contained therein only in a small amount. In addition, the paint may exhibit a gloss of not less than 85 %, an acid resistance ( $\Delta G$  value) of not more than 10.0 and a  $\Delta L^*$  value of not more than 1.0. In view of the blackness, the L\* value is preferably 15 to 18.5, more preferably 15 to 18; the gloss is preferably not less than 87 %, more preferably 88 %; the acid resistance represented by a  $\Delta G$  value is preferably not more than 9.5, more preferably not more than 9.3; and the  $\Delta L^*$  value is preferably not more than 0.9, more preferably not more than 0.8.

[0087] The water-based paint containing the black iron-based composite particles according to the present invention can exhibit a L\* value of 15 to 20 when formed into a coating film and, therefore, the blackness of the paint is substantially identical to the blackness of the carbon black fine particles solely, even when carbon black is contained therein only in a small amount. In addition, the paint can exhibit a gloss of not less than 80 %, an acid resistance ( $\Delta G$  value) of not more than 10.0 and a  $\Delta L^*$  value of not more than 1.0. In view of the blackness, the L\* value is preferably 15 to 19, more preferably 15 to 18; the gloss is preferably not less than 83 %, more preferably 85 %; the acid resistance represented by a  $\Delta G$  value is preferably not more than 9.5, more preferably not more than 9.0; and the  $\Delta L^*$  value is preferably not more than 0.9, more preferably not more than 0.8.

[0088] The blending percentage of the black iron-based composite particles in the paint according to the present invention is 1.0 to 100 parts by weight based on 100 parts by weight of a paint base material. In view of the handling property of the paint, the blending percentage of the black iron-based composite particles in the paint is preferably 2.0 to 100 parts by weight, more preferably 5.0 to 100 parts by weight.

[0089] The paint may contain as paint base materials, resins, solvents and if required, a defoamer, an extender pigment, a dryer, a surfactant, a hardener, auxiliaries and the like.

[0090] Examples of the resins for the solvent-based paint may include those ordinarily used therefor, such as acrylic resins, alkyd resins, polyester resins, polyurethane resins, epoxy resins, phenol resins, melamine resins, amino resins or the like. Examples of the resins for the water-based paint may also include those ordinarily used therefor, such as water-soluble alkyd resins, water-soluble melamine resins, water-soluble acrylic resins, water-soluble urethane emulsion resins or the like.

[0091] Examples of the solvents for the solvent-based paint may include those ordinarily used therefor, such as toluene, xylene, butyl acetate, methyl acetate, methyl isobutyl ketone, butyl cellosolve, ethyl cellosolve, butyl alcohol, hydrocarbons or the like.

[0092] As the solvents for the water-based paint, there may be exemplified those ordinarily used therefor, such as water containing butyl cellosolve, butyl alcohol or the like.

[0093] As the defoamer, there may be used commercially available products such as NOPCO 8034 (tradename), SN DEFOAMER 477 (tradename), SN DEFOAMER 5013 (tradename), SN DEFOAMER 247 (tradename) or SN DEFOAMER 382 (tradename) (all produced by SUN NOPCO LTD.); ANTIFOAM 08 (tradename) or EMULGEN 903 (tradename) (both produced by KAO CO., LTD.); or the like.

[0094] Next, the rubber or resin composition colored by the black iron-based composite particles according to the present invention is described.

[0095] The rubber or resin composition colored by the black iron-based composite particles according to the present invention has a L\* value of 15 to 21 and, therefore, can show a high blackness substantially identical to the blackness of the carbon black fine particles solely, even when carbon black is contained therein only in a small amount. In addition, the dispersibility measured by the visual observation is 4 or 5. With respect to the aging resistance, the percentage of discolored portions caused when the composition is heated at 190°C for 90 minutes is not more than 15 %. In view of the blackness, the L\* value is preferably 15 to 20, more preferably 15 to 19.5. The aging resistance is preferably not more than 10 %, more preferably not more than 5 %.

[0096] The blending percentage of the black iron-based composite particles in the rubber or resin composition according to the present invention is 0.5 to 200 parts by weight based on 100 parts by weight of base materials of the rubber or resin composition. In view of the handling property of the rubber or resin composition, the blending percentage of the black iron-based composite particles in the rubber or resin composition is 100 parts by weight.

[0097] The rubber or resin composition may contain as base materials, rubber, or known thermoplastic resins and

if required, additives such as a lubricant, a plasticizer, an antioxidant, an ultraviolet light absorber or various other stabilizers.

[0098] The additives may be added in an amount of not more than 50 % by weight based on the total weight of the black iron-based composite particles and the rubber or the resin. When the amount of the additives added is more than 50 % by weight, the rubber or resin composition is deteriorated in moldability.

[0099] The rubber or resin composition according to the present invention may be produced by preliminarily intimately mixing a raw rubber or resin material and the black iron-based composite particles together and applying a strong shear force to the mixture by a kneader or an extruder to diaggregate agglomerates of the black iron-based composite particles and uniformly disperse the individual black iron-based composite particles in the rubber or resin. The thus produced rubber or resin composition may be formed into an appropriate shape according to the application thereof upon use.

[0100] The important feature of the black iron-based composite particles according to the present invention exists at the following point. That is, the black iron oxide particles or the black iron oxide hydroxide particles whose surfaces may be coated, if required, with at least one compound selected from the group consisting of hydroxide of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon, are coated with the organosilicon compounds, and further carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$  are adhered on surfaces of a coating layer composed of the organosilicon compounds. The amount of the carbon black fine particles adhered is 1 to 30 parts by weight based on 100 parts by weight of the black iron oxide particles or the black iron oxide hydroxide particles. The thus obtained black iron-based composite particles are not only excellent in dispersibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the black iron-based composite particles, but also can show a blackness substantially identical to or not lower than the blackness obtained by using carbon black fine particles solely, even when carbon black is contained therein only in a small amount.

[0101] The reason why the black iron-based composite particles according to the present invention can show an excellent blackness, is considered as follows. That is, the carbon black fine particles which tend to be ordinarily aggregated due to the fineness thereof, can be uniformly and densely adhered on surfaces of the black iron oxide particles or the black iron oxide hydroxide particles through the organosilicon compounds applied on the core particles. For this reason, the dispersing condition of the carbon black fine particles is close to that of primary particles, thereby allowing the individual carbon black fine particles to effectively exhibit their blackness.

[0102] The reason why the amount of the carbon black fine particles desorbed from the surfaces of the black iron-based composite particles is small, is considered such that the organosilicon compounds onto which the carbon black fine particles are adhered, are strongly bonded to the surface of the black iron oxide particle or the black iron oxide hydroxide particle as a core particle.

[0103] Especially, in the case of using the alkoxysilane compounds or the fluoroalkylsilane compounds, metallosiloxane bonds ( $\text{=Si-O-M}$ , wherein M represents a metal atom contained in the black iron-based core particle, such as Si, Al or Fe) are formed between the metal elements such as Si, Al or Fe which are contained within the black iron oxide particle or the black iron oxide hydroxide particle or present at the surface thereof, and alkoxy groups of the alkoxysilane compounds or the fluoroalkylsilane compounds on which the carbon black fine particles are adhered, so that the organosilicon compounds onto which the carbon black fine particles are adhered, can be more strongly bonded to the surface of the black iron oxide particle or the black iron oxide hydroxide particle.

[0104] The reason why the black iron-based composite particles according to the present invention can show an excellent dispersibility in vehicles, or a rubber or resin composition, is considered as follows. That is, due to the fact that the amount of the carbon black fine particles desorbed from the surface of the black iron-based composite particle is small, it is unlikely that the dispersion in the system is inhibited by the carbon black fine particles desorbed. Further, since the carbon black fine particles are adhered on the surface of the black iron-based composite particle, irregularities are formed thereon, whereby the contact between the particles can be effectively prevented.

[0105] In addition, it is noted that a coating film having an excellent acid resistance and a rubber or resin composition having an excellent aging resistance can be obtained by using the black iron-based composite particles according to the present invention.

[0106] The reason why such a coating film having an excellent acid resistance, or such a rubber or resin composition having an excellent aging resistance can be obtained by using the black iron-based composite particles according to the present invention, is considered as follows. That is, since the carbon black fine particles which are inherently excellent in acid resistance and aging resistance, are adhered on the surfaces of the black iron oxide particles or the black iron oxide hydroxide particles through the organosilicon compounds, the inherent properties of the black iron oxide particles or the black iron oxide hydroxide particles such as a high oxidizability and a high surface activity can be eliminated. Thus, the inherent properties of the carbon black fine particles are effectively exhibited, so that the acid resistance of the coating film and the aging resistance of the rubber or resin composition can be enhanced.

[0107] The black iron-based composite particles according to the present invention can show an excellent dispers-

ibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the black iron-based composite particles and a high blackness substantially identical to the blackness of carbon black fine particles solely, even when carbon black is contained therein only in a small amount, and can provide a paint having an excellent acid resistance and a rubber or resin composition having an excellent aging resistance. As a result, the black iron-based composite particles can be advantageously used as black pigments for paints, printing ink, cosmetics, rubber or resin compositions, or the like.

[0108] The paint according to the present invention can exhibit a high blackness substantially identical to the blackness of carbon black fine particles solely, even when carbon black is contained therein only in a small amount, and can form a coating film having an excellent acid resistance. Therefore, the paint according to the present invention can be suitably used as a black paint.

[0109] The rubber or resin composition according to the present invention can also exhibit a high blackness substantially identical to the blackness of carbon black fine particles solely, even when carbon black is contained therein only in a small amount, and have an aging resistance. Therefore, the rubber or resin composition according to the present invention can be suitably used as a black rubber or resin composition.

[0110] Further, the black iron-based composite particles according to the present invention are excellent in dispersibility in a vehicle, and a rubber or resin composition and, therefore, can show excellent handling property or workability, thereby rendering these particles industrially and economically favorable.

[0111] Furthermore, since the amount of the carbon black fine particles used is small, the black iron-based composite particles according to the present invention are advantageous in view of safety and hygiene.

## EXAMPLES

[0112] The present invention will now be described in more detail with reference to the following examples, but the present invention is not restricted to those examples and various modifications are possible within the scope of the invention.

(1) The average particle sizes of black iron oxide particles, black iron oxide hydroxide particles, carbon black fine particles and black iron-based composite particles were respectively expressed by average values (measured in a predetermined direction) of about 350 particles which were sampled from a micrograph obtained by magnifying an original electron micrograph (x 20,000) by four times in each of the longitudinal and transverse directions.

(2) The aspect ratio of the particles was expressed by a ratio of average major axis diameter to minor axis diameter thereof.

(3) The geometrical standard deviation of particle sizes was expressed by values obtained by the following method. That is, the particle sizes were measured from the above magnified photograph. The actual particle sizes and the number of the particles were obtained from the calculation on the basis of the measured values. On a logarithmic normal probability paper, the particle sizes were plotted at regular intervals on the abscissa-axis and the cumulative number of particles belonging to each interval of the particle sizes were plotted by percentage on the ordinate-axis by a statistical technique. The particle sizes corresponding to the number of particles of 50 % and 84.13 %, respectively, were read from the graph, and the geometrical standard deviation was measured from the following formula:

Geometrical standard deviation =

$$\frac{\{\text{particle size corresponding to 84.13 \% under integration sieve}\}}{\{\text{particle size (geometrical average diameter) corresponding to 50 \% under integration sieve}\}}$$

The smaller the geometrical standard deviation, the more excellent the particle size distribution of the particles.

(4) The specific surface area was expressed by values measured by a BET method.

(5) The amounts of Mn, Al and Si which were present within black iron oxide particles, black iron oxide hydroxide particles and black iron-based composite particles or on surfaces thereof, and the amount of Si contained in organosilicon compounds, were measured by a fluorescent X-ray spectroscopy device 3063 (manufactured by RIGAKU DENKI KOGYO CO., LTD.) according to JIS K0119 "General rule of fluorescent X-ray analysis".

(6) The amount of carbon adhered (attached) on the black iron-based composite particles was measured by "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by HORIBA SEISAKUSHO CO., LTD.).

(7) The blackness of black iron oxide particles, black iron oxide hydroxide particles and black iron-based composite particles, were measured by the following method. That is, 0.5 g of sample particles and 0.7 cc of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately mixed to form a paint. The paint was applied on a cast-coated paper by using a 6-mil applicator to produce a coating film piece (having a film thickness of about 30  $\mu\text{m}$ ). The thus obtained coating film piece was measured according to JIS ZU8729 by a multi-light source spectrographic colorimeter MSC-IS-2D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) to determine a  $L^*$  value of colorimetric indices thereof.

(8) The blackness of each of paints containing black particles, was measured with respect to a coating film produced from the paint having the same composition as that of Example 2 or 3, and the blackness of each of rubber or resin compositions containing black particles, was measured with respect to a resin plate having the same composition as that of Example 4. The respective blackness was expressed by a  $L^*$  value of colorimetric indices which were measured according to JIS ZU8729 by a multi-light source spectrographic colorimeter MSC-IS-2D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.).

Here, the  $L^*$  value represents a lightness, and the smaller the  $L^*$  value, the more excellent the blackness.

(9) The dispersibility in a vehicle of paint was measured with respect to a coating film produced in the same manner as in Example 2 or 3, by examining the gloss on the surface of the coating film.

The gloss was measured by irradiating light at an incident angle of  $20^\circ$ , using a glossmeter UGV-5D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)

The higher the gloss, the more excellent the dispersibility.

(10) The viscosity (at  $25^\circ\text{C}$ ) of the paint prepared in the same manner as in Example 2 or 3, was measured at a shear rate ( $D$ ) of  $1.92 \text{ sec}^{-1}$  by E-type viscometer (cone plate-type viscometer) EMD-R (manufactured by TOKYO KEIKI CO., LTD.).

(11) The dispersibility in rubber or resin composition was evaluated by visually counting the number of undispersed aggregate particles on a surface of the rubber or resin composition obtained in the same manner as in Example 4 and classifying the results into the following five ranks. The 5th rank represents most excellent dispersing condition.

- Rank 1: not less than 50 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;
- Rank 2: 10 to 49 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;
- Rank 3: 5 to 9 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;
- Rank 4: 1 to 4 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;
- Rank 5: No undispersed aggregate particles were recognized.

(12) The acid resistance of a coating film was measured by the following method. That is, the paints containing the black particles, were applied onto a cold-rolled steel plate (having a size of  $0.8 \text{ mm} \times 70 \text{ mm} \times 150 \text{ mm}$ ; JIS G-3141) and then dried to prepare a sample on which a coating film having a thickness of  $150 \mu\text{m}$  was formed. The gloss and blackness of the thus prepared sample were measured.

Next, the sample was suspended by a thread and then was immersed by about 120 mm in depth into a 5 wt. % aqueous sulfuric acid solution of a temperature of  $25^\circ\text{C}$  in a 1,000 cc beaker. The sample was allowed to stand in the suspended condition for 24 hours.

Next, the sample was removed from the aqueous sulfuric acid solution and gently washed with flowing water. After water attached to the sample was removed by shaking, the gloss and blackness of the treated sample were measured at a central portion thereof. Based on the measured values of gloss and blackness before and after the immersion, the amount of change in gloss ( $\Delta G$  value) and the amount of change in blackness ( $\Delta L^*$  value) between before and after the immersion were obtained, thereby evaluating the acid resistance of the sample. The smaller both the  $\Delta G$  value and the  $\Delta L^*$  value, the more excellent the acid resistance.

(13) The aging resistance of a rubber or resin composition was measured by the following method. That is, colored resin plates (each having a size of  $1.5 \text{ cm}$  in length  $\times$   $1.5 \text{ cm}$  in width  $\times$   $1 \text{ mm}$  in thickness) in which the black particles were mixed and kneaded, were heated at  $190^\circ\text{C}$  to determine a surface area  $S$  of discolored portions thereof caused due to deterioration of the resin. The ratios of the discolored surface area  $S$  to a surface area  $S_0$  ( $1.5 \text{ cm} \times 1.5 \text{ cm} = 2.25 \text{ cm}^2$ ) of the resin plate before heating were determined and represented at intervals of 5 %.

That is, the condition that the percentage of  $(S/S_0) \times 100$  is 0 %, represents that no deterioration of resin was caused. On the other hand, the condition that the percentage of  $(S/S_0) \times 100$  is 100 %, represents that a whole portion of the resin was deteriorated.

(14) The desorption percentage (T %) of carbon black adhered on the black iron-based composite particles was measured by the following method.

That is, 3 g of the black iron-based composite particles and 40 ml of ethanol were placed in a 50-ml precipitation

pipe and then was subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, and separated the carbon black desorbed from the black iron-based composite particles on the basis of the difference in specific gravity therebetween. Next, the thus separated black iron-based composite particles were mixed again with 40 ml of ethanol, and the obtained mixture was further subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, thereby separating the black iron-based composite particles and carbon black desorbed from each other. The thus separated black iron-based composite particles were dried at 100°C for one hour, and then the carbon content thereof was measured by the "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by HORIBA SEISAKUSHO CO., LTD.). The desorption percentage (T %) was calculated according to the following formula:

$$T (\%) = \{(W_a - W_e)/W_a\} \times 100$$

wherein  $W_a$  represents an amount of carbon black initially adhered on the black iron-based composite particles; and  $W_e$  represents an amount of carbon black which still remains adhered on the black iron-based composite particles after the above desorption test.

The closer to zero the desorption percentage (T %), the smaller the amount of carbon black desorbed from the black iron-based composite particles.

#### Example 1:

##### <Production of black iron-based composite particles>

[0113] 20 kg of black manganese-containing hematite particles obtained according to the method described in Japanese Patent Application Laid-open (KOKAI) No. 4-144924(1992) and shown in the electron photograph (x 20,000) of Fig. 1 (particle shape: granular shape; average particle size: 0.30 μm; geometrical standard deviation of particle sizes: 1.46; BET specific surface area value: 3.6 m<sup>2</sup>/g; Mn content: 13.3 wt. %; and blackness (L\* value): 22.6), were aggregated in 150 liters of pure water using a stirrer, and further passed through a TK pipeline homomixer (manufactured by TOKUSHU KIKI KOGYO CO., LTD.) three times, to obtain a slurry containing the black manganese-containing hematite particles.

[0114] Successively, the obtained slurry was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by INOUE SEISAKUSHO CO., LTD.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the black manganese-containing hematite particles were dispersed.

[0115] The black manganese-containing hematite particles in the obtained slurry, which remain on a sieve of 325 meshes (mesh size: 44 μm) was 0 %. The slurry was filtered and washed with water, thereby obtaining a wet cake composed of the black manganese-containing hematite particles. The obtained wet cake composed of the black manganese-containing hematite particles was dried at 120°C. 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 30 Kg/cm for 30 minutes, thereby lightly aggregating the particles.

[0116] 110 g of methyl triethoxysilane was mixed and diluted with 200 ml of ethanol to obtain a solution of methyl triethoxysilane. The methyl triethoxysilane solution was added to the thus aggregated black manganese-containing hematite particles while operating the edge runner. The black manganese-containing hematite particles were continuously mixed and stirred at a linear load of 60 Kg/cm for 60 minutes.

[0117] Next, 990 g of carbon black fine particles as shown in the electron photograph (x 20,000) of Fig. 2 (particle shape: granular shape; particle size: 0.022 μm; geometrical standard deviation of particle sizes: 1.68; BET specific surface area value: 134 m<sup>2</sup>/g; and blackness (L\* value): 16.6), were added to the black manganese-containing hematite particles coated with methyl triethoxysilane for 10 minutes while operating the edge runner. Further, the particles were continuously mixed and stirred at a linear load of 60 Kg/cm for 60 minutes to adhere the carbon black fine particles on the coating layer composed of methyl triethoxysilane, thereby obtaining black iron-based composite particles.

[0118] The obtained black iron-based composite particles were dried or heat-treated at 105°C for 60 minutes by using a drier. The resultant black iron-based composite particles were granular particles having an average particle size of 0.31 μm as shown in the electron photograph (x 20,000) of Fig. 3. In addition, the black iron-based composite particles showed a geometrical standard deviation of particle sizes of 1.46, a BET specific surface area value of 9.1 m<sup>2</sup>/g, and a blackness (L\* value) of 17.6. The desorption percentage of carbon black fine particles from the black iron-based composite particles was 6.6 %. The amount of a coating organosilane compound produced from methyl triethoxysilane was 0.16 % by weight (calculated as Si). Since no carbon black fine particles were recognized on the electron photograph of Fig. 3, it was confirmed that a whole amount of the carbon black fine particles were adhered on the



coating layer composed of the organosilane compound produced from methyl triethoxysilane.

[0119] For a comparative purpose, the black manganese-containing hematite particles not coated with methyl triethoxysilane and the carbon black fine particles were mixed and stirred together by an edge runner in the same manner as described above, thereby obtaining treated particles as shown in the electron photograph (x 20,000) of Fig. 4. As shown in Fig. 4, it was recognized that the carbon black fine particles were not adhered on the black manganese-containing hematite particles, and the individual particles were present separately.

#### Example 2:

##### <Production of solvent-based paint containing black iron-based composite particles>

[0120] 10 g of the black iron-based composite particles produced in Example 1, were blended with an amino alkyd resin and a thinner at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mmφ glass beads. Next, the obtained mixture was mixed and dispersed for 90 minutes by a paint shaker, thereby preparing a mill base.

Composition of Mill Base:	
Black iron-based composite particles	12.2 parts by weight
Amino alkyd resin (AMILAC No. 1026, produced by KANSAI PAINT CO., LTD.)	19.5 parts by weight
Thinner	7.3 parts by weight

[0121] The above-prepared mill base was blended with an amino alkyd resin at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a paint containing the black iron-based composite particles.

Composition of paint:	
Mill base	39.0 parts by weight
Amino alkyd resin (AMILAC No. 1026, produced by KANSAI PAINT CO., LTD.)	51.0 parts by weight

[0122] The coating film produced from the thus obtained paint, showed a gloss of 89 % and a blackness ( $L^*$  value) of 17.4. Further, as a result of an acid resistance test thereof, the amount of change in gloss ( $\Delta G$  value) was 5.6 %, and the amount of change in lightness ( $\Delta L^*$  value) was 0.6.

#### Example 3:

##### <Production of water-based paint containing black iron-based composite particles>

[0123] 7.62 g of the black iron-based composite particles obtained in Example 1, were blended with a water-soluble alkyd resin and the like at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mmφ glass beads. Next, the obtained mixture was mixed and dispersed for 45 minutes or 90 minutes by a paint shaker, thereby preparing a mill base.

Composition of Mill Base:	
Black iron-based composite particles	12.4 parts by weight
Water-soluble alkyd resin (tradename: "S-118", produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	9.0 parts by weight
Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)	4.8 parts by weight
Water	4.8 parts by weight
Butyl cellosolve	4.1 parts by weight

[0124] The above-prepared mill base was blended with paint components at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a water-soluble paint.

Composition of paint:		
5	Mill base	30.4 parts by weight
	Water-soluble alkyd resin (tradename: S-118, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	46.2 parts by weight
10	Water-soluble melamine resin (tradename: S-695, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	12.6 parts by weight
	Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)	0.1 parts by weight
	Water	9.1 parts by weight
	Butyl cellosolve	1.6 parts by weight

[0125] The coating film prepared from the thus obtained paint, showed a gloss of 37 % and a blackness ( $L^*$  value) of 17.4. Further, as a result of an acid resistance test thereof, the amount of change in gloss ( $\Delta G$  value) was 5.1 %, and the amount of change in lightness ( $\Delta L^*$  value) was 0.6.

#### Example 4:

##### <Production of resin composition>

[0126] 2.5 g of the black iron-based composite particles obtained in Example 1, and 47.5 g of a polyvinyl chloride resin 103EP6D (produced by NIPPON ZEON CO., LTD.) were weighed and charged into a 100 ml beaker, and intimately mixed together by a spatula, thereby obtaining mixed particles.

[0127] 0.5 g of calcium stearate was added to the mixed particles. The mixed particles were intimately mixed and then slowly supplied to hot rolls heated to 160°C whose clearance was set to 0.2 mm, and continuously kneaded therebetween until a uniform resin composition was produced. The resin composition kneaded was separated from the hot rolls and used as a raw material for forming a colored resin plate.

[0128] Next, the thus-produced resin composition was interposed between a pair of surface-polished stainless steel plates, placed within a hot press heated to 180°C and subjected to a pressure molding while applying a pressure of 1 ton/cm<sup>2</sup> thereto, thereby obtaining a colored resin plate having a thickness of 1 mm. The thus-produced colored resin plate had a blackness ( $L^*$  value) of 17.9 and the dispersing condition thereof was the rank 5.

[0129] The colored resin plate was cut into three 1.5 cm-square test pieces. The three test pieces were placed in Geer oven maintained heated to 190°C and taken out therefrom one by one at intervals of 30 minutes to examine whether or not the resin of each test piece was deteriorated. As a result, the test piece taken out 30 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, the test piece next taken out 60 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 5 %, and the test piece lastly taken out 90 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 5 %.

##### Core particles 1 to 7:

[0130] Various black iron oxide particles and black iron oxide hydroxide particles produced by known methods, were prepared. The same procedure as defined in Example 1 was conducted by using these particles, thereby obtaining diagggregated black iron oxide particles and black iron oxide hydroxide particles.

[0131] Various properties of the thus obtained black iron oxide particles and black iron oxide hydroxide particles are shown in Table 1.

[0132] Meanwhile, the core particles 1 and 2 were produced by the method described in Japanese Patent Application Laid-open (KOKAI) No. 4-144924(1992). The core particles 3 were produced by the method described in Japanese Patent Publication (KOKOKU) No. 44-668(1969). The core particles 4 were produced by the method described in Japanese Patent Publication (KOKOKU) No. 3-9045(1991). The core particles 5 were produced by first preparing acicular goethite particles and then heat-treating the obtained acicular goethite particles at 340°C in air, followed by heat-treating the acicular goethite particles at 400°C in a hydrogen stream by the method described in Japanese Patent Publication (KOKOKU) No. 55-6579(1980). Further, the core particles 6 and 7 were produced by the method described in Japanese Patent Application Laid-open (KOKAI) No. 6-263449(1994).

##### Core particles 8:

[0133] The same procedure as defined in Example 1 was conducted by using 20 kg of the diagggregated black man-

ganese-containing hematite particles (core particles 1) and 150 liters of water, thereby obtaining a slurry containing the black manganese-containing hematite particles. The pH value of the obtained re-dispersed slurry containing the black manganese-containing hematite particles was adjusted to 10.5, and then the concentration of the solid content in the slurry was adjusted to 98 g/liter by adding water thereto. After 150 liters of the slurry was heated to 60°C, 2722 ml of a 1.0 mol/liter NaAlO<sub>2</sub> solution (corresponding to 0.5 % by weight (calculated as Al) based on the weight of the black manganese-containing hematite particles) was added to the slurry. After allowing the obtained slurry to stand for 30 minutes, the pH value of the slurry was adjusted to 7.5 by using acetic acid. After further allowing the resultant slurry to stand for 30 minutes, the slurry was subjected to filtration, washing with water, drying and pulverization, thereby obtaining the black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum.

[0134] The thus obtained black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum were granular particles having a particle size of 0.32 µm. The geometrical standard deviation of particle sizes of the obtained particles was 1.47, the BET specific surface area value was 3.8 m<sup>2</sup>/g, and the blackness (L\* value) was 22.6. As a result of fluorescent X-ray analysis, the obtained particles had a Mn content of 13.0 % by weight and an Al content of 0.49 % by weight.

#### Core particles 9 to 14:

[0135] The same procedure as defined above for the production of the core particles 8, was conducted except that kinds of core particles and kinds and amounts of additives used in the above surface treatment were changed variously, thereby obtaining surface-treated black iron oxide particles and surface-treated black iron oxide hydroxide particles.

[0136] The essential treating conditions are shown in Table 2, and various properties of the obtained surface-treated core particles are shown in Table 3.

#### Examples 5 to 11 and Comparative Examples 1 to 5:

[0137] The same procedure as defined in Example 1 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, addition or non-addition of alkoxysilane, kinds and amounts of alkoxysilane added, treating conditions of an edge runner used in the alkoxysilane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 5 to 11. Therefore, it was confirmed that a substantially whole amount of the carbon black fine particles used in Examples 5 to 11 were adhered on the coating layer composed of an organosilane compound produced from the alkoxysilane.

[0138] Various properties of the carbon black fine particles A to C used, are shown in Table 4. The essential treating conditions are shown in Table 5, and various properties of the obtained black iron-based composite particles are shown in Table 6.

#### Example 12:

[0139] 11.0 kg of the core particles 8, i.e., the black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum, were charged into an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 30 kg/cm for 30 minutes, thereby diaggregating the particles.

[0140] 220 g of methyl triethoxysilane was mixed and diluted with 400 ml of ethanol to prepare a solution of methyl triethoxysilane. The thus prepared methyl triethoxysilane solution was added to the diaggregated black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum while operating the edge runner. The black manganese-containing hematite particles were continuously mixed and stirred at a linear load of 60 kg/cm for 30 minutes.

[0141] Next, 1,100 g of the carbon black fine particles A were added to the black manganese-containing hematite particles coated with methyl triethoxysilane, for 10 minutes while operating the edge runner. Further, the particles were continuously mixed and stirred at a linear load of 75 kg/cm for 30 minutes to adhere the carbon black fine particles on the coating layer composed of methyl triethoxysilane, thereby obtaining black iron-based composite particles.

[0142] The obtained black iron-based composite particles were heat-treated at 105°C for 60 minutes by using a drier. The black iron-based composite particles were granular particles having a particle size of 0.32 µm. In addition, the geometrical standard deviation of particle sizes of the obtained black iron-based composite particles was 1.44; the BET specific surface area value was 4.6 m<sup>2</sup>/g; the blackness (L\* value) was 16.5; the desorption percentage of carbon black was 4.8 %. The coating amount of the organosilane compound produced from methyl triethoxysilane was 0.31

% by weight (calculated as Si). Meanwhile, since almost no carbon black fine particles were recognized as a result of the observation by an electron microscope, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of the organosilane compound produced from methyl triethoxysilane

#### Examples 13 to 18:

[0143] The same procedure as defined in Example 12 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of alkoxysilane added, treating conditions of an edge runner used in the alkoxysilane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 13 to 18. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of a organosilane compound produced from the alkoxysilane.

[0144] The essential treating conditions are shown in Table 5, and various properties of the obtained black iron-based composite particles are shown in Table 6.

#### Comparative Example 6 (Method described in Japanese Patent Publication (KOKOKU) No. 50-13300(1975)):

[0145] 1,000 ml of a water suspension containing 68.3 g of the core particles 3, i.e., magnetite particles (black iron oxide particles) was prepared, and then washed with cold water five times.

[0146] Next, 5 g of a water dispersion containing 1.75 g of the dried carbon black fine particles B was diluted with 500 ml of cold water.

[0147] While stirring, the carbon black-containing water dispersion was added to the water suspension containing the magnetite particles, for 5 minutes. After completion of the addition, the mixed suspension was continuously stirred for 10 minutes and then allowed to stand.

[0148] After about 4 hours, the obtained black precipitates were washed with water five times by an ordinary method, and then dried at 100°C in air.

[0149] The obtained black particles had a blackness (L\* value) of 20.0 which was substantially unchanged from those of the magnetite particles as the core particles and a carbon black desorption percentage of 50.2 %.

#### Examples 19 to 32 and Comparative Examples 7 to 21:

##### <Production of solvent-based paint>

[0150] The same procedure as defined in Example 2 was conducted except that kinds of black particles were changed variously, thereby obtaining solvent-based paints.

[0151] The essential production conditions and various properties of coating films obtained from the solvent-based paints are shown in Tables 7 and 8, respectively.

#### Examples 33 to 46 and Comparative Examples 22 to 36:

##### <Production of water-based paint>

[0152] The same procedure as defined in Example 3 was conducted except that kinds of black particles were changed variously, thereby obtaining water-based paints.

[0153] The essential production conditions and various properties of coating films obtained from the water-based paints are shown in Tables 9 and 10, respectively.

#### Examples 47 to 60 and Comparative Examples 37 to 51: <Production of resin composition>

[0154] The same procedure as defined in Example 4 was conducted except that kinds of black particles were changed variously, thereby obtaining resin compositions.

[0155] The essential production conditions and various properties of colored resin plates obtained from the resin compositions are shown in Tables 11 and 12, respectively.

Example 61:

[0156] 110 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by TOSHIBA SILICONE CO., LTD.) was added to the disaggregated black manganese-containing hematite particles obtained in Example 1, while operating an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and then continuously mixed and stirred at a linear load of 60 kg/cm for 60 minutes.

[0157] Next, 550 g of carbon black fine particles (particle shape: granular shape; particle size: 0.022  $\mu\text{m}$ ; geometrical standard deviation of particle sizes: 1.68; BET specific surface area value: 134  $\text{m}^2/\text{g}$ ; and blackness ( $L^*$  value): 16.6) were added to the black manganese-containing hematite particles coated with methyl hydrogen polysiloxane, for 10 minutes while operating the edge runner. Further, the obtained particles were continuously mixed and stirred at a linear load of 60 kg/cm for 60 minutes to adhere the carbon black fine particles on the coating layer composed of methyl hydrogen polysiloxane, thereby obtaining black iron-based composite particles.

[0158] The obtained black iron-based composite particles were dried at 105°C for 60 minutes by using a drier. The obtained black iron-based composite particles were granular particles having an particle size of 0.31  $\mu\text{m}$ . In addition, the geometrical standard deviation of particle sizes of the black iron-based composite particles was 1.46; the BET specific surface area value was 3.9  $\text{m}^2/\text{g}$ ; the blackness ( $L^*$  value) was 18.2; the carbon black desorption percentage was 6.4 %. The coating amount of the methyl hydrogen polysiloxane was 0.41 % by weight (calculated as Si). As a result of the observation by an electron microscope, since almost no carbon black fine particles were recognized in the obtained composite particles, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of the methyl hydrogen polysiloxane.

Example 62:

[0159] The same procedure as defined in Example 2 was conducted except that black iron-based composite particles obtained in Example 61 were used, thereby obtaining a solvent-based paint.

[0160] A coating film obtained from the solvent-based paint had a gloss of 91 % and a blackness ( $L^*$  value) of 18.6. As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 6.1 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.7.

Example 63:

[0161] The same procedure as defined in Example 3 was conducted except that black iron-based composite particles obtained in Example 61 were used, thereby obtaining a water-based paint.

[0162] A coating film obtained from the water-based paint had a gloss of 86 % and a blackness ( $L^*$  value) of 18.8. As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 5.3 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.7.

Example 64:

[0163] The same procedure as defined in Example 4 was conducted except that black iron-based composite particles obtained in Example 61 were used, thereby obtaining a colored resin plate. The thus obtained colored resin plate had a blackness ( $L^*$  value) of 17.9 and the dispersion condition thereof was the rank 5.

[0164] The colored resin plate was cut into three 1.5 cm-square test pieces. The three test pieces were placed in Geer oven maintained at 190°C and were taken out therefrom one by one at intervals of 30 minutes to examine whether or not the resin of each test piece was deteriorated. As a result, the test piece taken out 30 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, the test piece next taken out 60 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, and the test piece lastly taken out 90 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 5 %.

Examples 65 to 71 and Comparative Examples 52 to 54:

[0165] The same procedure as defined in Example 61 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of polysiloxane added, treating conditions of an edge runner used in the polysiloxane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 65 to 71. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were

adhered on the coating layer composed of polysiloxane.

[0166] The essential treating conditions are shown in Table 13, and various properties of the obtained black iron-based composite particles are shown in Table 14.

#### Example 72:

[0167] 11.0 kg of the core particles 8, i.e., the black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum, were charged into an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 30 kg/cm for 30 minutes, thereby diaggregating the particles.

[0168] 165 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by TOSHIBA SILICONE CO., LTD.) were added to the diaggregated black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum while operating the edge runner. The black manganese-containing hematite particles were continuously mixed and stirred at a linear load of 30 kg/cm for 30 minutes.

[0169] Next, 550 g of the carbon black fine particles A were added to the black manganese-containing hematite particles coated with methyl hydrogen polysiloxane, for 10 minutes while operating the edge runner. Further, the particles were continuously mixed and stirred at a linear load of 75 kg/cm for 30 minutes to adhere the carbon black fine particles on the coating layer composed of methyl hydrogen polysiloxane, thereby obtaining black iron-based composite particles.

[0170] The obtained black iron-based composite particles were dried at 105°C for 60 minutes by using a drier. The black iron-based composite particles were granular particles having an particle size of 0.32 µm. In addition, the geometrical standard deviation of particle sizes of the obtained black iron-based composite particles was 1.45; the BET specific surface area value was 4.1 m<sup>2</sup>/g; the blackness (L\* value) was 16.9; the desorption percentage of carbon black was 4.9 %. The coating amount of the methyl hydrogen polysiloxane was 0.65 % by weight (calculated as Si). Meanwhile, since almost no carbon black fine particles were recognized as a result of the observation by an electron microscope, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of the methyl hydrogen polysiloxane.

#### Examples 73 to 78:

[0171] The same procedure as defined in Example 72 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of polysiloxane added, treating conditions of an edge runner used in the polysiloxane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 73 to 78. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of a polysiloxane.

[0172] The essential treating conditions are shown in Table 13, and various properties of the obtained black iron-based composite particles are shown in Table 14.

#### Examples 79 to 92 and Comparative Examples 55 to 57:

##### <Production of solvent-based paint>

[0173] The same procedure as defined in Example 2 was conducted except that kinds of black particles were changed variously, thereby obtaining solvent-based paints.

[0174] The essential production conditions and various properties of coating films obtained from the solvent-based paints are shown in Table 15.

#### Examples 93 to 106 and Comparative Examples 58 to 60:

##### <Production of water-based paint>

[0175] The same procedure as defined in Example 3 was conducted except that kinds of black particles were changed variously, thereby obtaining water-based paints.

[0176] The essential production conditions and various properties of coating films obtained from the water-based paints are shown in Table 16.

Examples 107 to 120 and Comparative Examples 61 to 63:<Production of resin composition>

[0177] The same procedure as defined in Example 4 was conducted except that kinds of black particles were changed variously, thereby obtaining resin compositions.

[0178] The essential production conditions and various properties of colored resin plates obtained from the resin compositions are shown in Table 17.

Example 121:

[0179] 110 g of polyether-modified polysiloxane (tradename "BYK-080", produced by BYK-Chemie CO., LTD.) were added to the diaggregated black manganese-containing hematite particles obtained in Example 1, while operating an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and then continuously mixed and stirred at a linear load of 60 kg/cm for 60 minutes.

[0180] Next, 550 g of carbon black fine particles (particle shape: granular shape; particle size: 0.022  $\mu\text{m}$ ; geometrical standard deviation of particle sizes: 1.68; BET specific surface area: 134  $\text{m}^2/\text{g}$ ; and blackness ( $L^*$  value): 16.6) were added to the black manganese-containing hematite particles coated with polyether-modified polysiloxane, for 10 minutes while operating the edge runner. Further, the obtained particles were continuously mixed and stirred at a linear load of 60 kg/cm for 60 minutes to adhere the carbon black fine particles on the coating layer composed of polyether-modified polysiloxane, thereby obtaining black iron-based composite particles.

[0181] The obtained black iron-based composite particles was dried at 105°C for 60 minutes by using a drier. The obtained black iron-based composite particles were granular particles having an particle size of 0.31  $\mu\text{m}$ . In addition, the geometrical standard deviation of particle sizes of the black iron-based composite particles was 1.46; the BET specific surface area value was 4.6  $\text{m}^2/\text{g}$ ; the blackness ( $L^*$  value) was 17.6; the carbon black desorption percentage was 6.2 %. The coating amount of the polyether-modified polysiloxane was 0.19 % by weight (calculated as Si). As a result of the observation by an electron microscope, since almost no carbon black fine particles were recognized in the obtained composite particles, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of the polyether-modified polysiloxane.

Example 122:

[0182] The same procedure as defined in Example 2 was conducted except that black iron-based composite particles obtained in Example 121, were used, thereby obtaining a solvent-based paint.

[0183] A coating film obtained from the solvent-based paint had a gloss of 101 % and a blackness ( $L^*$  value) of 17.2. As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 6.3 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.6.

Example 123:

[0184] The same procedure as defined in Example 3 was conducted except that black iron-based composite particles obtained in Example 121 were used, thereby obtaining a water-based paint.

[0185] A coating film obtained from the water-based paint had a gloss of 92 % and a blackness ( $L^*$  value) of 17.8. As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 6.1 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.8.

Example 124:

[0186] The same procedure as defined in Example 4 was conducted except that black iron-based composite particles obtained in Example 121 were used, thereby obtaining a colored resin plate. The thus obtained colored resin plate had a blackness ( $L^*$  value) of 18.0 and the dispersion condition thereof was the rank 5.

[0187] The colored resin plate was cut into three 1.5 cm-square test pieces. The three test pieces were placed in Geer oven maintained at 190°C and were taken out therefrom one by one at intervals of 30 minutes to examine whether or not the resin of each test piece was deteriorated. As a result, the test piece taken out 30 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, the test piece next taken out 60 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, and the test piece lastly taken out 90 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 5 %.

Examples 125 to 131 and Comparative Examples 64 to 66:

[0188] The same procedure as defined in Example 121 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of modified polysiloxane added, treating conditions of an edge runner used in the modified polysiloxane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 125 to 131. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of modified polysiloxane.

[0189] The essential treating conditions are shown in Table 18, and various properties of the obtained black iron-based composite particles are shown in Table 19.

Example 132:

[0190] 11.0 kg of the core particles 8, i.e., the black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum, were charged into an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 30 kg/cm for 30 minutes, thereby diaggregating the particles.

[0191] 220 g of polyether-modified polysiloxane (tradename "BYK-080", produced by BYK-Chemie CO., LTD.) were added to the diaggregated black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum while operating the edge runner. The black manganese-containing hematite particles were continuously mixed and stirred at a linear load of 75 kg/cm for 15 minutes.

[0192] Next, 550 g of the carbon black fine particles A were added to the black manganese-containing hematite particles coated with polyether-modified polysiloxane, for 10 minutes while operating the edge runner. Further, the particles were continuously mixed and stirred at a linear load of 60 kg/cm for 30 minutes to adhere the carbon black fine particles on the coating layer composed of polyether-modified polysiloxane, thereby obtaining black iron-based composite particles.

[0193] The obtained black iron-based composite particles was dried at 105°C for 60 minutes by using a drier. The black iron-based composite particles were granular particles having an particle size of 0.32  $\mu\text{m}$ . In addition, the geometrical standard deviation of particle sizes of the obtained black iron-based composite particles was 1.44; the BET specific surface area value was 4.6  $\text{m}^2/\text{g}$ ; the blackness ( $L^*$  value) was 16.5; the desorption percentage of carbon black was 4.1 %. The coating amount of the polyether-modified polysiloxane was 0.36 % by weight (calculated as Si). Meanwhile, since almost no carbon black fine particles were recognized as a result of the observation by an electron microscope, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of polyether-modified polysiloxane.

Examples 133 to 138:

[0194] The same procedure as defined in Example 132 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of modified polysiloxane added, treating conditions of an edge runner used in the modified polysiloxane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 133 to 138. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of a modified polysiloxane.

[0195] The essential treating conditions are shown in Table 18, and various properties of the obtained black iron-based composite particles are shown in Table 19.

Examples 139 to 152 and Comparative Examples 67 to 69:<Production of solvent-based paint>

[0196] The same procedure as defined in Example 2 was conducted except that kinds of black particles were changed variously, thereby obtaining solvent-based paints.

[0197] The essential production conditions and various properties of coating films obtained from the solvent-based paints are shown in Table 20.



Examples 153 to 166 and Comparative Examples 70 to 72:<Production of water-based paint>

**[0198]** The same procedure as defined in Example 3 was conducted except that kinds of black particles were changed variously, thereby obtaining water-based paints.

**[0199]** The essential production conditions and various properties of coating films obtained from the water-based paints are shown in Table 21.

Examples 167 to 180 and Comparative Examples 73 to 75:<Production of resin composition>

**[0200]** The same procedure as defined in Example 4 was conducted except that kinds of black particles were changed variously, thereby obtaining resin compositions.

**[0201]** The essential production conditions and various properties of colored resin plates obtained from the resin compositions are shown in Table 22.

Example 181:

**[0202]** 220 g of carboxylic acid-terminal-modified polysiloxane (tradename: "TSF4770", produced by TOSHIBA SILICONE CO., LTD.) was added to the aggregated black manganese-containing hematite particles obtained in Example 1, while operating an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and then continuously mixed and stirred at a linear load of 60 kg/cm for 30 minutes.

**[0203]** Next, 550 g of carbon black fine particles (particle shape: granular shape; particle size: 0.022  $\mu\text{m}$ ; geometrical standard deviation of particle sizes: 1.68; BET specific surface area value: 134  $\text{m}^2/\text{g}$ ; and blackness ( $L^*$  value): 16.6) were added to the black manganese-containing hematite particles coated with carboxylic acid-terminal-modified polysiloxane, for 10 minutes while operating the edge runner. Further, the obtained particles were continuously mixed and stirred at a linear load of 60 kg/cm for 30 minutes to adhere the carbon black fine particles on the coating layer composed of carboxylic acid-terminal-modified polysiloxane, thereby obtaining black iron-based composite particles.

**[0204]** The obtained black iron-based composite particles was dried at 105°C for 60 minutes by using a drier. The obtained black iron-based composite particles were granular particles having an particle size of 0.32  $\mu\text{m}$ . In addition, the geometrical standard deviation of particle sizes of the black iron-based composite particles was 1.46; the BET specific surface area value was 4.2  $\text{m}^2/\text{g}$ ; the blackness ( $L^*$  value) was 17.9; the carbon black desorption percentage was 6.7 %. The coating amount of the carboxylic acid-terminal-modified polysiloxane was 0.43 % by weight (calculated as Si). As a result of the observation by an electron microscope, since almost no carbon black fine particles were recognized in the obtained composite particles, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of carboxylic acid-terminal-modified polysiloxane.

Example 182:

**[0205]** The same procedure as defined in Example 2 was conducted except that black iron-based composite particles obtained in Example 181 were used, thereby obtaining a solvent-based paint.

**[0206]** A coating film obtained from the solvent-based paint had a gloss of 98 % and a blackness ( $L^*$  value) of 17.8. As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 7.1 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.7.

Example 183:

**[0207]** The same procedure as defined in Example 3 was conducted except that black iron-based composite particles obtained in Example 181 were used, thereby obtaining a water-based paint.

**[0208]** A coating film obtained from the water-based paint had a gloss of 93 % and a blackness ( $L^*$  value) of 18.1. As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 7.3 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.8.

Example 184:

**[0209]** The same procedure as defined in Example 4 was conducted except that black iron-based composite particles

obtained in Example 181 were used, thereby obtaining a colored resin plate. The thus obtained colored resin plate had a blackness ( $L^*$  value) of 18.0 and the dispersion condition thereof was the rank 5.

[0210] The colored resin plate was cut into three 1.5 cm-square test pieces. The three test pieces were placed in Geer oven maintained at 190°C and were taken out therefrom one by one at intervals of 30 minutes to examine whether or not the resin of each test piece was deteriorated. As a result, the test piece taken out 30 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, the test piece next taken out 60 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, and the test piece lastly taken out 90 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 5 %.

#### Examples 185 to 191 and Comparative Examples 76 to 78:

[0211] The same procedure as defined in Example 181 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of terminal-modified polysiloxane added, treating conditions of an edge runner used in the terminal-modified polysiloxane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 185 to 191. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of terminal-modified polysiloxane.

[0212] The essential treating conditions are shown in Table 23, and various properties of the obtained black iron-based composite particles are shown in Table 44.

#### Example 192:

[0213] 11.0 kg of the core particles 8, i.e., the black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum, were charged into an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 30 kg/cm for 30 minutes, thereby diaggregating the particles.

[0214] 110 g of carboxylic acid-terminal-modified polysiloxane was added to the diaggregated black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum while operating the edge runner. The black manganese-containing hematite particles were continuously mixed and stirred at a linear load of 30 kg/cm for 45 minutes.

[0215] Next, 825 g of the carbon black fine particles A were added to the black manganese-containing hematite particles coated with carboxylic acid-terminal-modified polysiloxane, for 10 minutes while operating the edge runner. Further, the particles were continuously mixed and stirred at a linear load of 45 kg/cm for 45 minutes to adhere the carbon black fine particles on the coating layer composed of carboxylic acid-terminal-modified polysiloxane, thereby obtaining black iron-based composite particles.

[0216] The obtained black iron-based composite particles was dried at 105°C for 60 minutes by using a drier. The black iron-based composite particles were granular particles having a particle size of 0.32  $\mu\text{m}$ . In addition, the geometrical standard deviation of particle sizes of the obtained black iron-based composite particles was 1.44; the BET specific surface area value was 5.1  $\text{m}^2/\text{g}$ ; the blackness ( $L^*$  value) was 16.6; the desorption percentage of carbon black was 3.6 %. The coating amount of carboxylic acid-terminal-modified polysiloxane was 0.21 % by weight (calculated as Si). Meanwhile, since almost no carbon black fine particles were recognized as a result of the observation by an electron microscope, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of the carboxylic acid-terminal-modified polysiloxane.

#### Examples 193 to 198:

[0217] The same procedure as defined in Example 192 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of terminal-modified polysiloxane added, treating conditions of an edge runner used in the terminal-modified polysiloxane-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 193 to 198. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of a terminal-modified polysiloxane.

[0218] The essential treating conditions are shown in Table 23, and various properties of the obtained black iron-based composite particles are shown in Table 24.

Examples 199 to 212 and Comparative Examples 79 to 81:<Production of solvent-based paint>

[0219] The same procedure as defined in Example 2 was conducted except that kinds of black particles were changed variously, thereby obtaining solvent-based paints.

[0220] The essential production conditions and various properties of coating films obtained from the solvent-based paints are shown in Table 25.

Examples 213 to 226 and Comparative Examples 82 to 84:<Production of water-based paint>

[0221] The same procedure as defined in Example 3 was conducted except that kinds of black particles were changed variously, thereby obtaining water-based paints.

[0222] The essential production conditions and various properties of coating films obtained from the water-based paints are shown in Table 26.

Examples 227 to 240 and Comparative Examples 85 to 87:<Production of resin composition>

[0223] The same procedure as defined in Example 4 was conducted except that kinds of black particles were changed variously, thereby obtaining resin compositions.

[0224] The essential production conditions and various properties of colored resin plates obtained from the resin compositions are shown in Table 27.

Example 241:

[0225] 165 g of tridecafluorooctyl trimethoxysilane (tradename "TSL8257", produced by TOSHIBA SILICONE CO., LTD.) were added to the diaggregated black manganese-containing hematite particles obtained in Example 1, while operating an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and then continuously mixed and stirred at a linear load of 60 kg/cm for 30 minutes.

[0226] Next, 550 g of carbon black fine particles (particle shape: granular shape; particle size: 0.022  $\mu\text{m}$ ; geometrical standard deviation of particle sizes: 1.68; BET specific surface area value: 134  $\text{m}^2/\text{g}$ ; and blackness ( $L^*$  value): 16.6) were added to the black manganese-containing hematite particles coated with tridecafluorooctyl trimethoxysilane, for 10 minutes while operating the edge runner. Further, the obtained particles were continuously mixed and stirred at a linear load of 60 kg/cm for 30 minutes to adhere the carbon black fine particles on the coating layer composed of tridecafluorooctyl trimethoxysilane, thereby obtaining black iron-based composite particles.

[0227] The obtained black iron-based composite particles was dried or heat-treated at 105°C for 60 minutes by using a drier. The obtained black iron-based composite particles were granular particles having an particle size of 0.31  $\mu\text{m}$ . In addition, the geometrical standard deviation of particle sizes of the black iron-based composite particles was 1.45; the BET specific surface area value was 5.0  $\text{m}^2/\text{g}$ ; the blackness ( $L^*$  value) was 17.8; the carbon black desorption percentage was 6.5 %. The coating amount of the fluoroalkyl organosilane compound produced from tridecafluorooctyl trimethoxysilane was 0.10 % by weight (calculated as Si). As a result of the observation by an electron microscope, since almost no carbon black fine particles were recognized in the obtained composite particles, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of the fluoroalkyl organosilane compound produced from tridecafluoroalkyl trimethoxysilane.

Example 242:

[0228] The same procedure as defined in Example 2 was conducted except that black iron-based composite particles obtained in Example 241 were used, thereby obtaining a solvent-based paint.

[0229] A coating film obtained from the solvent-based paint had a gloss of 96 % and a blackness ( $L^*$  value) of 17.3.

As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 7.2 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.7.

Example 243:

[0230] The same procedure as defined in Example 3 was conducted except that black iron-based composite particles obtained in Example 241 were used, thereby obtaining a water-based paint.

[0231] A coating film obtained from the water-based paint had a gloss of 91 % and a blackness ( $L^*$  value) of 17.9. As a result of an acid resistance test of the coating film, the amount of change in gloss ( $\Delta G$  value) was 8.3 % and the amount of change in lightness ( $\Delta L^*$  value) was 0.7.

Example 244:

[0232] The same procedure as defined in Example 4 was conducted except that black iron-based composite particles obtained in Example 241 were used, thereby obtaining a colored resin plate. The thus obtained colored resin plate had a blackness ( $L^*$  value) of 18.0 and the dispersion condition thereof was the rank 5.

[0233] The colored resin plate was cut into three 1.5 cm-square test pieces. The three test pieces were placed in Geer oven maintained at 190°C and were taken out therefrom one by one at intervals of 30 minutes to examine whether or not the resin of each test piece was deteriorated. As a result, the test piece taken out 30 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 0 %, the test piece next taken out 60 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 5 %, and the test piece lastly taken out 90 minutes after initiation of the heating showed a degree of resin-deterioration ( $S/S_0 \times 100$ ) of 5 %.

Examples 245 to 251 and Comparative Examples 88 to 90:

[0234] The same procedure as defined in Example 241 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of fluoroalkyl silane compounds added, treating conditions of an edge runner used in the fluoroalkyl silane compound-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 245 to 251. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of fluoroalkyl organosilane compounds.

[0235] The essential treating conditions are shown in Table 28, and various properties of the obtained black iron-based composite particles are shown in Table 29.

Example 252:

[0236] 11.0 kg of the core particles 8, i.e., the black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum, were charged into an edge runner "MPUV-2 Model" (manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 30 kg/cm for 30 minutes, thereby diaggregating the particles.

[0237] 660 g of tridecafluorooctyl trimethoxysilane (tradename "TSL-8257", produced by TOSHIBA SILICONE CO., LTD.) was added to the diaggregated black manganese-containing hematite particles whose surface was coated with hydroxides of aluminum while operating the edge runner. The black manganese-containing hematite particles were continuously mixed and stirred at a linear load of 75 kg/cm for 30 minutes.

[0238] Next, 1,100 g of the carbon black fine particles A were added to the black manganese-containing hematite particles coated with tridecafluorooctyl trimethoxysilane, for 10 minutes while operating the edge runner. Further, the particles were continuously mixed and stirred at a linear load of 60 kg/cm for 45 minutes to adhere the carbon black fine particles on the coating layer composed of tridecafluorooctyl trimethoxysilane, thereby obtaining black iron-based composite particles.

[0239] The obtained black iron-based composite particles was dried or heat-treated at 105°C for 60 minutes by using a drier. The black iron-based composite particles were granular particles having an particle size of 0.32  $\mu\text{m}$ . In addition, the geometrical standard deviation of particle sizes of the obtained black iron-based composite particles was 1.48; the BET specific surface area value was 4.8  $\text{m}^2/\text{g}$ ; the blackness ( $L^*$  value) was 16.6; the desorption percentage of carbon black was 3.6 %. The coating amount of the fluoroalkyl organosilane compound produced from tridecafluorooctyl trimethoxysilane was 0.40 % by weight (calculated as Si). Meanwhile, since almost no carbon black fine particles were recognized as a result of the observation by an electron microscope, it was confirmed that substantially a whole amount of the carbon black fine particles were adhered on the coating layer composed of the fluoroalkyl organosilane compound produced from tridecafluorooctyl trimethoxysilane.

Examples 253 to 258:

[0240] The same procedure as defined in Example 252 was conducted except that kinds of black iron oxide particles and black iron oxide hydroxide particles, kinds and amounts of fluoroalkylsilane compound added, treating conditions of an edge runner used in the fluoroalkylsilane compound-coating process, kinds and amounts of carbon black fine particles adhered, and treating conditions of an edge runner used in the process for adhering the carbon black fine particles, were changed variously, thereby obtaining black iron-based composite particles. As a result of the observation by an electron microscope, almost no carbon black fine particles were recognized in the black iron-based composite particles obtained in Examples 253 to 258. Therefore, it was confirmed that substantially a whole amount of the carbon black fine particles used were adhered on the coating layer composed of a fluoroalkyl organosilane compound produced from fluoroalkylsilane compounds.

[0241] The essential treating conditions are shown in Table 28, and various properties of the obtained black iron-based composite particles are shown in Table 29.

Examples 259 to 272 and Comparative Examples 91 to 93:<Production of solvent-based paint>

[0242] The same procedure as defined in Example 2 was conducted except that kinds of black particles were changed variously, thereby obtaining solvent-based paints.

[0243] The essential production conditions and various properties of coating films obtained from the solvent-based paints are shown in Table 30.

Examples 273 to 286 and Comparative Examples 94 to 96:<Production of water-based paint>

[0244] The same procedure as defined in Example 3 was conducted except that kinds of black particles were changed variously, thereby obtaining water-based paints.

[0245] The essential production conditions and various properties of coating films obtained from the water-based paints are shown in Table 31.

Examples 297 to 300 and Comparative Examples 97 to 99:<Production of resin composition>

[0246] The same procedure as defined in Example 4 was conducted except that kinds of black particles were changed variously, thereby obtaining resin compositions.

[0247] The essential production conditions and various properties of colored resin plates obtained from the resin compositions are shown in Table 32.

Table 1

Core particles	Properties of black iron oxide particles or black iron oxide hydroxide particles	
	Kinds	Particle shape
Core particles 1	Manganese-containing hematite particles	Granular
Core particles 2	Manganese-containing hematite particles	Granular
Core particles 3	Magnetite particles	Octahedral
Core particles 4	Magnetite particles	Spherical
Core particles 5	Magnetite particles	Acicular
Core particles 6	Manganese-containing goethite particles	Acicular
Core particles 7	Manganese-containing hematite particles	Spindle-shaped

Table 1 (continued)

Core particles	Properties of black iron oxide particles or black iron oxide hydroxide particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Core particles 1	0.32	-	-	1.49
Core particles 2	0.18	-	-	1.41
Core particles 3	0.28	-	-	1.53
Core particles 4	0.23	-	-	1.35
Core particles 5	0.40	0.051	7.8	1.53
Core particles 6	0.28	0.038	7.3	1.38
Core particles 7	0.20	0.030	6.7	1.41

Table 1 (continued)

Core particles	Properties of black iron oxide particles or black iron oxide hydroxide particles		
	BET specific surface area (m <sup>2</sup> /g)	Mn content (wt. %)	Blackness (L* value) (-)
Core particles 1	3.1	13.1	22.4
Core particles 2	7.8	15.6	24.4
Core particles 3	4.6	-	20.3
Core particles 4	11.8	-	20.1
Core particles 5	18.8	-	23.8
Core particles 6	84.3	17.6	26.5
Core particles 7	45.8	13.6	24.9

Table 2

Core particles	Kind of core particles	Surface-treating process		
		Additives		
		Kinds	Calculated as	Amount (wt. %)
Core particles 8	Core particles 1	Sodium aluminate	Al	0.5
Core particles 9	Core particles 2	Water glass #3	SiO <sub>2</sub>	0.2
Core particles 10	Core particles 3	Aluminum sulfate	Al	1.5
		Water glass #3	SiO <sub>2</sub>	0.5
Core particles 11	Core particles 4	Sodium aluminate	Al	2.0
		Colloidal silica	SiO <sub>2</sub>	1.0
Core particles 12	Core particles 5	Aluminum acetate	Al	5.0
Core particles 13	Core particles 6	Aluminum sulfate	Al	1.0
Core particles 14	Core particles 7	Sodium aluminate	Al	1.0

Table 2 (continued)

Core particles	Surface-treating process		
	Coating material		
	Kinds	Calculated as	Amount (wt. %)
Core particles 8	A	Al	0.49
Core particles 9	S	SiO <sub>2</sub>	0.18
Core particles 10	A	Al	1.46
	S	SiO <sub>2</sub>	0.49
Core particles 11	A	Al	1.92
	S	SiO <sub>2</sub>	0.96
Core particles 12	A	Al	4.75
Core particles 13	A	Al	0.98
Core particles 14	A	Al	0.98

Note; A: Hydroxide of aluminum

S: Oxide of silicon



Table 3

Core particles	Properties of surface-treated core particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Core particles 8	0.32	-	-	1.47
Core particles 9	0.18	-	-	1.40
Core particles 10	0.29	-	-	1.51
Core particles 11	0.24	-	-	1.35
Core particles 12	0.40	0.051	7.8	1.52
Core particles 13	0.28	0.038	7.3	1.38
Core particles 14	0.20	0.030	6.7	1.41

Table 3 (continued)

Core particles	Properties of surface-treated core particles		
	BET specific surface area ( $\text{m}^2/\text{g}$ )	Mn content (wt. %)	Blackness ( $L^*$ value) (-)
Core particles 8	3.8	13.0	22.6
Core particles 9	7.5	15.6	25.1
Core particles 10	9.8	-	21.4
Core particles 11	13.6	-	20.8
Core particles 12	25.4	-	24.6
Core particles 13	81.9	17.5	26.7
Core particles 14	45.8	13.4	24.8

Table 4

Kind of carbon black particles	Properties of carbon black fine particles		
	Particle shape	Average particle size ( $\mu\text{m}$ )	Geometrical standard deviation (-)
Carbon black A	Granular	0.022	1.78
Carbon black B	Granular	0.015	1.56
Carbon black C	Granular	0.030	2.06

Table 4 (continued)

Kind of carbon black particles	Properties of carbon black fine particles		
	BET specific surface area ( $\text{m}^2/\text{g}$ )	Oil absorption ( $\text{ml}/100\text{g}$ )	Blackness ( $L^*$ value) (-)
Carbon black A	133.5	84	14.6
Carbon black B	265.3	57	15.2
Carbon black C	84.6	95	17.0

Table 5

Examples and Comparative Examples	Kind of core particles	Production of black iron-based composite particles or black iron-based particles	
		Addition of alkoxysilane compound or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 5	Core particles 1	Methyl triethoxysilane	1.0
Example 6	Core particles 2	Methyl trimethoxysilane	2.0
Example 7	Core particles 3	Dimethyl dimethoxysilane	1.0
Example 8	Core particles 4	Phenyl triethoxysilane	0.5
Example 9	Core particles 5	Isobutyl trimethoxysilane	5.0
Example 10	Core particles 6	Methyl triethoxysilane	3.0
Example 11	Core particles 7	Methyl triethoxysilane	1.5
Example 12	Core particles 8	Methyl triethoxysilane	2.0
Example 13	Core particles 9	Methyl trimethoxysilane	5.0
Example 14	Core particles 10	Dimethyl dimethoxysilane	0.2
Example 15	Core particles 11	Phenyl triethoxysilane	1.5
Example 16	Core particles 12	Isobutyl trimethoxysilane	1.0
Example 17	Core particles 13	Methyl triethoxysilane	3.0
Example 18	Core particles 14	Methyl triethoxysilane	1.5
Comparative Example 1	Core particles 1	-	-
Comparative Example 2	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 3	Core particles 3	Dimethyl dimethoxysilane	0.5
Comparative Example 4	Core particles 3	Methyl triethoxysilane	0.005
Comparative Example 5	Core particles 1	$\gamma$ -aminopropyl triethoxysilane	1.0

Table 5 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of alkoxysilane compound or silicon compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 5	60	30	0.16
Example 6	60	30	0.41
Example 7	45	15	0.22
Example 8	75	20	0.06
Example 9	30	60	0.73
Example 10	60	30	0.46
Example 11	60	60	0.24
Example 12	60	30	0.31
Example 13	60	15	0.97
Example 14	60	20	0.05
Example 15	30	60	0.18
Example 16	45	30	0.16
Example 17	45	30	0.46
Example 18	30	30	0.24
Comparative Example 1	-	-	-
Comparative Example 2	60	20	0.15
Comparative Example 3	60	30	0.11
Comparative Example 4	60	30	$7.9 \times 10^{-4}$
Comparative Example 5	60	30	0.13

Table 5 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles	
	Addition of carbon black fine particles	
	Carbon black fine particles	
	Kinds	Amount added (part by weight)
Example 5	A	9.0
Example 6	A	5.0
Example 7	B	6.0
Example 8	B	12.0
Example 9	C	16.0
Example 10	C	18.0
Example 11	C	13.0
Example 12	A	10.0
Example 13	A	15.0
Example 14	B	20.0
Example 15	B	15.0
Example 16	C	10.0
Example 17	C	18.0
Example 18	C	17.0
Comparative Example 1	A	10.0
Comparative Example 2	-	-
Comparative Example 3	A	0.01
Comparative Example 4	B	5.0
Comparative Example 5	C	10.0

Table 5 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 5	60	30	8.30
Example 6	60	20	4.75
Example 7	30	60	5.66
Example 8	30	90	10.73
Example 9	45	45	13.70
Example 10	60	60	15.19
Example 11	60	30	11.49
Example 12	75	30	9.05
Example 13	60	30	13.04
Example 14	30	45	16.63
Example 15	60	60	12.99
Example 16	60	30	9.09
Example 17	60	30	15.25
Example 18	60	30	14.53
Comparative Example 1	60	30	9.06
Comparative Example 2	-	-	-
Comparative Example 3	30	60	0.01
Comparative Example 4	60	45	4.75
Comparative Example 5	60	30	9.00

Table 6

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Example 5	0.32	-	-	1.46
Example 6	0.18	-	-	1.40
Example 7	0.28	-	-	1.52
Example 8	0.24	-	-	1.34
Example 9	0.41	0.053	7.8	1.51
Example 10	0.28	0.038	7.3	1.39
Example 11	0.20	0.030	6.7	1.41
Example 12	0.32	-	-	1.44
Example 13	0.19	-	-	1.38
Example 14	0.30	-	-	1.47
Example 15	0.24	-	-	1.34
Example 16	0.40	0.051	7.8	1.50
Example 17	0.28	0.038	7.3	1.38
Example 18	0.19	0.028	6.7	1.42
Comparative Example 1	0.33	-	-	1.47
Comparative Example 2	0.32	-	-	1.47
Comparative Example 3	0.28	-	-	1.52
Comparative Example 4	0.28	-	-	1.52
Comparative Example 5	0.33	-	-	1.47

Table 6 (continued)

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	BET specific surface area (m <sup>2</sup> /g)	Mn content (wt. %)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 5	5.1	12.0	16.3	6.8
Example 6	7.6	14.6	17.8	7.2
Example 7	5.0	-	17.0	8.6
Example 8	13.6	-	16.4	5.6
Example 9	23.8	-	17.8	9.1
Example 10	91.6	14.6	17.8	8.3
Example 11	47.6	11.9	17.6	6.8
Example 12	4.6	11.6	16.5	4.8
Example 13	9.1	13.0	16.8	1.6
Example 14	14.4	-	15.9	3.9
Example 15	16.1	-	16.2	4.8
Example 16	24.8	-	17.5	4.0
Example 17	86.4	14.4	17.2	2.3
Example 18	48.1	11.5	17.3	0.9
Comparative Example 1	16.6	12.0	21.3	68.3
Comparative Example 2	4.6	13.1	23.1	-
Comparative Example 3	5.6	-	21.4	-
Comparative Example 4	17.6	-	20.1	46.8
Comparative Example 5	10.7	11.9	22.0	51.6



Table 7

Examples	Production of solvent-based paint		Properties of paint
	Kinds of black iron-based composite particles	Kinds of resin	Viscosity (cP)
Example 19	Example 5	Aminoalkyd resin	640
Example 20	Example 6	Aminoalkyd resin	845
Example 21	Example 7	Aminoalkyd resin	712
Example 22	Example 8	Aminoalkyd resin	640
Example 23	Example 9	Aminoalkyd resin	896
Example 24	Example 10	Aminoalkyd resin	998
Example 25	Example 11	Aminoalkyd resin	712
Example 26	Example 12	Aminoalkyd resin	538
Example 27	Example 13	Aminoalkyd resin	793
Example 28	Example 14	Aminoalkyd resin	768
Example 29	Example 15	Aminoalkyd resin	614
Example 30	Example 16	Aminoalkyd resin	712
Example 31	Example 17	Aminoalkyd resin	793
Example 32	Example 18	Aminoalkyd resin	768

Table 7 (continued)

Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 19	103	15.6	6.7	0.6
Example 20	108	16.6	9.3	0.7
Example 21	96	16.3	8.2	0.8
Example 22	103	16.1	6.6	0.7
Example 23	88	17.5	8.3	0.6
Example 24	118	17.4	8.6	0.8
Example 25	121	17.4	6.8	0.7
Example 26	106	16.4	3.6	0.2
Example 27	113	16.4	4.5	0.3
Example 28	103	15.6	2.1	0.3
Example 29	103	16.0	1.6	0.2
Example 30	91	17.1	3.2	0.3
Example 31	125	17.0	4.8	0.3
Example 32	128	17.2	3.6	0.3

Table 8

Comparative Examples	Production of solvent-based paint		Properties of paint
	Kinds of black particles	Kinds of resin	Viscosity (cP)
Comparative Example 7	Core particles 1	Aminoalkyd resin	538
Comparative Example 8	Core particles 2	Aminoalkyd resin	896
Comparative Example 9	Core particles 3	Aminoalkyd resin	640
Comparative Example 10	Core particles 4	Aminoalkyd resin	793
Comparative Example 11	Core particles 5	Aminoalkyd resin	972
Comparative Example 12	Core particles 6	Aminoalkyd resin	1,178
Comparative Example 13	Carbon black A	Aminoalkyd resin	8,192
Comparative Example 14	Carbon black B	Aminoalkyd resin	10,240
Comparative Example 15	Carbon black C	Aminoalkyd resin	6,400
Comparative Example 16	Comparative Example 1	Aminoalkyd resin	3,840
Comparative Example 17	Comparative Example 2	Aminoalkyd resin	435
Comparative Example 18	Comparative Example 3	Aminoalkyd resin	972
Comparative Example 19	Comparative Example 4	Aminoalkyd resin	4,352
Comparative Example 20	Comparative Example 5	Aminoalkyd resin	3,584
Comparative Example 21	Comparative Example 6	Aminoalkyd resin	2,816

Table 8 (continued)

Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Comparative Example 7	76	21.9	12.8	1.5
Comparative Example 8	82	23.8	14.6	1.6
Comparative Example 9	69	20.1	12.8	2.2
Comparative Example 10	78	19.8	16.1	1.4
Comparative Example 11	61	21.2	13.1	1.9
Comparative Example 12	80	26.1	12.6	1.5
Comparative Example 13	43	14.8	11.6	1.2
Comparative Example 14	21	15.6	10.8	1.2
Comparative Example 15	56	16.3	10.2	1.4
Comparative Example 16	61	21.2	12.6	1.3
Comparative Example 17	80	22.0	10.3	1.6
Comparative Example 18	72	20.5	11.0	1.3
Comparative Example 19	46	19.6	12.2	1.2
Comparative Example 20	58	22.0	11.3	1.2
Comparative Example 21	61	21.6	11.8	1.3

Table 9

Examples	Production of water-based paint		Properties of paint
	Kinds of black iron-based composite particles	Kinds of resin	Viscosity (cP)
Example 33	Example 5	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 34	Example 6	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 35	Example 7	Water-soluble alkyd resin Water-soluble melamine resin	768
Example 36	Example 8	Water-soluble alkyd resin Water-soluble melamine resin	845
Example 37	Example 9	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 38	Example 10	Water-soluble alkyd resin Water-soluble melamine resin	922
Example 39	Example 11	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 40	Example 12	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 41	Example 13	Water-soluble alkyd resin Water-soluble melamine resin	614
Example 42	Example 14	Water-soluble alkyd resin Water-soluble melamine resin	666
Example 43	Example 15	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 44	Example 16	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 45	Example 17	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 46	Example 18	Water-soluble alkyd resin Water-soluble melamine resin	768

Table 9 (continued)

Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 33	91	16.7	8.9	0.8
Example 34	97	17.5	8.5	0.8
Example 35	91	17.1	8.4	0.7
Example 36	95	17.8	7.4	0.8
Example 37	86	18.4	8.1	0.7
Example 38	110	17.6	7.8	0.7
Example 39	115	17.5	8.3	0.8
Example 40	98	17.5	4.6	0.4
Example 41	101	17.4	4.1	0.4
Example 42	96	16.7	3.5	0.3
Example 43	95	17.2	2.6	0.4
Example 44	88	18.3	4.1	0.4
Example 45	118	17.2	3.6	0.3
Example 46	116	17.6	3.8	0.4

Table 10

Comparative Examples	Production of water-based paint		Properties of paint
	Kinds of black particles	Kinds of resin	Viscosity (cP)
Comparative Example 22	Core particles 1	Water-soluble alkyd resin Water-soluble melamine resin	870
Comparative Example 23	Core particles 2	Water-soluble alkyd resin Water-soluble melamine resin	1,050
Comparative Example 24	Core particles 3	Water-soluble alkyd resin Water-soluble melamine resin	819
Comparative Example 25	Core particles 4	Water-soluble alkyd resin Water-soluble melamine resin	922
Comparative Example 26	Core particles 5	Water-soluble alkyd resin Water-soluble melamine resin	998
Comparative Example 27	Core particles 6	Water-soluble alkyd resin Water-soluble melamine resin	1,152
Comparative Example 28	Carbon black A	Water-soluble alkyd resin Water-soluble melamine resin	12,800
Comparative Example 29	Carbon black B	Water-soluble alkyd resin Water-soluble melamine resin	16,640
Comparative Example 30	Carbon black C	Water-soluble alkyd resin Water-soluble melamine resin	8,704
Comparative Example 31	Comp. Ex. 1	Water-soluble alkyd resin Water-soluble melamine resin	2,995
Comparative Example 32	Comp. Ex. 2	Water-soluble alkyd resin Water-soluble melamine resin	788
Comparative Example 33	Comp. Ex. 3	Water-soluble alkyd resin Water-soluble melamine resin	1,024
Comparative Example 34	Comp. Ex. 4	Water-soluble alkyd resin Water-soluble melamine resin	3,174
Comparative Example 35	Comp. Ex. 5	Water-soluble alkyd resin Water-soluble melamine resin	3,328
Comparative Example 36	Comp. Ex. 6	Water-soluble alkyd resin Water-soluble melamine resin	2,560

Table 10 (continued)

Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Comparative Example 22	73	22.4	16.9	1.8
Comparative Example 23	76	24.1	18.3	2.4
Comparative Example 24	65	21.0	16.6	3.0
Comparative Example 25	70	20.6	21.5	2.1
Comparative Example 26	48	21.8	18.7	2.4
Comparative Example 27	74	26.0	15.8	2.3
Comparative Example 28	20	16.1	14.6	1.4
Comparative Example 29	15	16.3	12.8	1.6
Comparative Example 30	9	16.9	12.1	1.5
Comparative Example 31	58	22.1	15.8	1.9
Comparative Example 32	68	23.2	12.1	2.0
Comparative Example 33	64	21.4	13.0	1.6
Comparative Example 34	38	20.7	14.3	1.7
Comparative Example 35	60	21.9	13.8	1.8
Comparative Example 36	48	22.6	14.1	2.0



Table 11

Examples	Production of resin composition	
	Black iron-based composite particles	
	Kinds	Amount (part by weight)
Example 47	Example 5	5.0
Example 48	Example 6	5.0
Example 49	Example 7	5.0
Example 50	Example 8	5.0
Example 51	Example 9	5.0
Example 52	Example 10	5.0
Example 53	Example 11	5.0
Example 54	Example 12	5.0
Example 55	Example 13	5.0
Example 56	Example 14	5.0
Example 57	Example 15	5.0
Example 58	Example 16	5.0
Example 59	Example 17	5.0
Example 60	Example 18	5.0

Table 11 (continued)

Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Example 47	Polyvinyl chloride resin	95.0
Example 48	Polyvinyl chloride resin	95.0
Example 49	Polyvinyl chloride resin	95.0
Example 50	Polyvinyl chloride resin	95.0
Example 51	Polyvinyl chloride resin	95.0
Example 52	Polyvinyl chloride resin	95.0
Example 53	Polyvinyl chloride resin	95.0
Example 54	Polyvinyl chloride resin	95.0
Example 55	Polyvinyl chloride resin	95.0
Example 56	Polyvinyl chloride resin	95.0
Example 57	Polyvinyl chloride resin	95.0
Example 58	Polyvinyl chloride resin	95.0
Example 59	Polyvinyl chloride resin	95.0
Example 60	Polyvinyl chloride resin	95.0

Table 11 (continued)

Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Example 47	Calcium stearate	1.0	160
Example 48	Calcium stearate	1.0	160
Example 49	Calcium stearate	1.0	160
Example 50	Calcium stearate	1.0	160
Example 51	Calcium stearate	1.0	160
Example 52	Calcium stearate	1.0	160
Example 53	Calcium stearate	1.0	160
Example 54	Calcium stearate	1.0	160
Example 55	Calcium stearate	1.0	160
Example 56	Calcium stearate	1.0	160
Example 57	Calcium stearate	1.0	160
Example 58	Calcium stearate	1.0	160
Example 59	Calcium stearate	1.0	160
Example 60	Calcium stearate	1.0	160

Table 11 (continued)

Examples	Properties of resin composition				
	Dispers- ing condition	Blacknes s (L* value)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S <sub>0</sub> ) x 100 (%)		
			30 minutes	60 minutes	90 minutes
	(-)	(-)			
Example 47	5	17.5	0	5	5
Example 48	4	18.7	0	5	10
Example 49	5	18.4	0	5	5
Example 50	4	18.8	0	0	5
Example 51	4	19.5	0	5	10
Example 52	4	18.7	0	0	5
Example 53	5	18.9	0	0	5
Example 54	5	18.6	0	0	5
Example 55	5	18.8	0	0	0
Example 56	5	17.6	0	0	5
Example 57	5	18.0	0	0	0
Example 58	5	18.5	0	0	0
Example 59	5	18.2	0	0	0
Example 60	5	18.1	0	0	0

Table 12

Comparative Examples	Production of resin composition	
	Black particles	
	Kinds	Amount (part by weight)
Comparative Example 37	Core particles 1	5.0
Comparative Example 38	Core particles 2	5.0
Comparative Example 39	Core particles 3	5.0
Comparative Example 40	Core particles 4	5.0
Comparative Example 41	Core particles 5	5.0
Comparative Example 42	Core particles 6	5.0
Comparative Example 43	Carbon black A	5.0
Comparative Example 44	Carbon black B	5.0
Comparative Example 45	Carbon black C	5.0
Comparative Example 46	Comparative Example 1	5.0
Comparative Example 47	Comparative Example 2	5.0
Comparative Example 48	Comparative Example 3	5.0
Comparative Example 49	Comparative Example 4	5.0
Comparative Example 50	Comparative Example 5	5.0
Comparative Example 51	Comparative Example 6	5.0

Table 12 (continued)

Comparative Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Comparative Example 37	Polyvinyl chloride resin	95.0
Comparative Example 38	Polyvinyl chloride resin	95.0
Comparative Example 39	Polyvinyl chloride resin	95.0
Comparative Example 40	Polyvinyl chloride resin	95.0
Comparative Example 41	Polyvinyl chloride resin	95.0
Comparative Example 42	Polyvinyl chloride resin	95.0
Comparative Example 43	Polyvinyl chloride resin	95.0
Comparative Example 44	Polyvinyl chloride resin	95.0
Comparative Example 45	Polyvinyl chloride resin	95.0
Comparative Example 46	Polyvinyl chloride resin	95.0
Comparative Example 47	Polyvinyl chloride resin	95.0
Comparative Example 48	Polyvinyl chloride resin	95.0
Comparative Example 49	Polyvinyl chloride resin	95.0
Comparative Example 50	Polyvinyl chloride resin	95.0
Comparative Example 51	Polyvinyl chloride resin	95.0

Table 12 (continued)

Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Comparative Example 37	Calcium stearate	1.0	160
Comparative Example 38	Calcium stearate	1.0	160
Comparative Example 39	Calcium stearate	1.0	160
Comparative Example 40	Calcium stearate	1.0	160
Comparative Example 41	Calcium stearate	1.0	160
Comparative Example 42	Calcium stearate	1.0	160
Comparative Example 43	Calcium stearate	1.0	160
Comparative Example 44	Calcium stearate	1.0	160
Comparative Example 45	Calcium stearate	1.0	160
Comparative Example 46	Calcium stearate	1.0	160
Comparative Example 47	Calcium stearate	1.0	160
Comparative Example 48	Calcium stearate	1.0	160
Comparative Example 49	Calcium stearate	1.0	160
Comparative Example 50	Calcium stearate	1.0	160
Comparative Example 51	Calcium stearate	1.0	160

Table 12 (continued)

Comparative Examples	Properties of resin composition				
	Dispers- ing condition  (-)	Blackness (L* value)  (-)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S <sub>0</sub> ) × 100 (%)		
			30 minutes	60 minutes	90 minutes
Comparative Example 37	3	24.6	15	30	50
Comparative Example 38	2	26.1	30	60	85
Comparative Example 39	3	22.4	15	35	60
Comparative Example 40	3	22.4	10	20	40
Comparative Example 41	3	24.8	5	20	60
Comparative Example 42	2	27.5	5	15	25
Comparative Example 43	2	17.8	5	10	35
Comparative Example 44	2	18.6	5	10	15
Comparative Example 45	3	19.3	10	20	25
Comparative Example 46	3	23.2	10	20	35
Comparative Example 47	3	24.3	10	15	25
Comparative Example 48	3	22.7	10	15	30
Comparative Example 49	3	21.5	15	25	35
Comparative Example 50	3	23.5	10	20	30
Comparative Example 51	2	23.8	10	15	25



Table 13

Examples and Comparative Examples	Kind of core particles	Production of black iron-based composite particles or black iron-based particles	
		Addition of polysiloxane	
		Additives	
		Kinds	Amount added (part by weight)
Example 65	Core particles 1	TSF484	1.0
Example 66	Core particles 2	TSF484	5.0
Example 67	Core particles 3	KF99	2.0
Example 68	Core particles 4	L-9000	1.0
Example 69	Core particles 5	TSF484/TSF451	0.4/0.1
Example 70	Core particles 6	TSF484/L-45	0.5/1.5
Example 71	Core particles 7	TSF451	3.0
Example 72	Core particles 8	TSF484	1.5
Example 73	Core particles 9	TSF484	3.5
Example 74	Core particles 10	KF99	1.0
Example 75	Core particles 11	L-9000	2.0
Example 76	Core particles 12	TSF484/TSF451	0.25 /0.05
Example 77	Core particles 13	TSF484/L-45	1.0/4.0
Example 78	Core particles 14	TSF451	2.0
Comparative Example 52	Core particles 1	TSF484	1.0
Comparative Example 53	Core particles 2	TSF484	0.5
Comparative Example 54	Core particles 3	TSF484	0.005

Table 13 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 65	60	30	0.44
Example 66	45	45	2.19
Example 67	60	30	0.87
Example 68	30	30	0.45
Example 69	75	30	0.23
Example 70	60	30	0.75
Example 71	45	30	1.10
Example 72	30	60	0.65
Example 73	45	45	1.51
Example 74	45	30	0.43
Example 75	30	30	0.87
Example 76	60	30	0.13
Example 77	60	60	1.89
Example 78	30	45	0.75
Comparative Example 52	60	30	0.44
Comparative Example 53	60	30	0.21
Comparative Example 54	60	30	$2.2 \times 10^{-3}$

Table 13 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles	
	Addition of carbon black fine particles	
	Carbon black fine particles	
	Kinds	Amount added (part by weight)
Example 65	A	10.0
Example 66	A	3.0
Example 67	A	5.0
Example 68	B	10.0
Example 69	B	15.0
Example 70	C	5.0
Example 71	C	8.0
Example 72	A	5.0
Example 73	A	10.0
Example 74	A	15.0
Example 75	B	10.0
Example 76	B	20.0
Example 77	C	7.5
Example 78	C	10.0
Comparative Example 52	-	-
Comparative Example 53	A	0.01
Comparative Example 54	B	3.0

Table 13 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 65	60	60	9.06
Example 66	60	20	2.90
Example 67	45	30	4.75
Example 68	30	30	9.11
Example 69	60	30	13.01
Example 70	30	60	4.76
Example 71	60	45	7.41
Example 72	75	30	4.72
Example 73	60	30	8.99
Example 74	60	60	12.89
Example 75	45	45	9.08
Example 76	30	90	16.56
Example 77	30	60	6.98
Example 78	60	20	9.05
Comparative Example 52	-	-	-
Comparative Example 53	60	45	0.01
Comparative Example 54	60	45	2.91

Table 14

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Example 65	0.32	-	-	1.47
Example 66	0.18	-	-	1.40
Example 67	0.28	-	-	1.53
Example 68	0.23	-	-	1.35
Example 69	0.41	0.053	7.8	1.52
Example 70	0.29	0.040	7.3	1.38
Example 71	0.21	0.031	6.7	1.41
Example 72	0.32	-	-	1.45
Example 73	0.18	-	-	1.39
Example 74	0.29	-	-	1.52
Example 75	0.23	-	-	1.34
Example 76	0.40	0.051	7.8	1.50
Example 77	0.28	0.038	7.3	1.38
Example 78	0.19	0.028	6.7	1.41
Comparative Example 52	0.32	-	-	1.48
Comparative Example 53	0.28	-	-	1.52
Comparative Example 54	0.28	-	-	1.52

Table 14 (continued)

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	BET specific surface area (m <sup>2</sup> /g)	Mn content (wt. %)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 65	6.2	11.9	16.2	5.8
Example 66	8.3	15.0	17.9	6.9
Example 67	5.6	-	17.2	5.2
Example 68	12.8	-	16.6	6.8
Example 69	21.6	-	17.9	8.4
Example 70	86.6	16.6	17.9	7.1
Example 71	47.1	12.5	17.7	6.9
Example 72	4.1	12.3	16.9	4.9
Example 73	7.9	14.1	17.1	3.2
Example 74	13.6	-	16.1	4.3
Example 75	15.5	-	16.5	2.6
Example 76	19.6	-	16.9	0.8
Example 77	86.3	16.4	17.6	1.6
Example 78	46.6	12.2	17.7	2.1
Comparative Example 52	4.5	13.1	23.1	-
Comparative Example 53	6.1	-	21.4	-
Comparative Example 54	17.8	-	20.5	48.3

Table 15

Examples and Comparative Examples	Production of solvent-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 79	Example 65	Aminoalkyd resin	768
Example 80	Example 66	Aminoalkyd resin	845
Example 81	Example 67	Aminoalkyd resin	794
Example 82	Example 68	Aminoalkyd resin	717
Example 83	Example 69	Aminoalkyd resin	666
Example 84	Example 70	Aminoalkyd resin	923
Example 85	Example 71	Aminoalkyd resin	870
Example 86	Example 72	Aminoalkyd resin	640
Example 87	Example 73	Aminoalkyd resin	666
Example 88	Example 74	Aminoalkyd resin	717
Example 89	Example 75	Aminoalkyd resin	589
Example 90	Example 76	Aminoalkyd resin	666
Example 91	Example 77	Aminoalkyd resin	742
Example 92	Example 78	Aminoalkyd resin	845
Comparative Example 55	Comparative Example 2	Aminoalkyd resin	384
Comparative Example 56	Comparative Example 3	Aminoalkyd resin	896
Comparative Example 57	Comparative Example 4	Aminoalkyd resin	4,122

Table 15 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 79	100	15.6	6.9	0.7
Example 80	102	16.7	8.9	0.7
Example 81	98	16.5	8.5	0.8
Example 82	100	16.2	6.8	0.6
Example 83	123	17.6	8.1	0.6
Example 84	116	17.4	7.9	0.7
Example 85	91	17.4	9.8	0.9
Example 86	109	16.6	3.2	0.3
Example 87	115	16.8	3.8	0.1
Example 88	106	15.7	2.3	0.2
Example 89	112	16.3	2.0	0.2
Example 90	109	16.8	1.5	0.2
Example 91	97	17.1	4.7	0.3
Example 92	99	17.5	4.6	0.4
Comparative Example 55	76	22.2	10.9	1.3
Comparative Example 56	73	20.7	11.3	1.4
Comparative Example 57	38	19.8	12.5	1.4



Table 16

Examples and Comparative Examples	Production of water-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 93	Example 65	Water-soluble alkyd resin Water-soluble melamine resin	845
Example 94	Example 66	Water-soluble alkyd resin Water-soluble melamine resin	793
Example 95	Example 67	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 96	Example 68	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 97	Example 69	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 98	Example 70	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 99	Example 71	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 100	Example 72	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 101	Example 73	Water-soluble alkyd resin Water-soluble melamine resin	768
Example 102	Example 74	Water-soluble alkyd resin Water-soluble melamine resin	640
Example 103	Example 75	Water-soluble alkyd resin Water-soluble melamine resin	691
Example 104	Example 76	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 105	Example 77	Water-soluble alkyd resin Water-soluble melamine resin	947
Example 106	Example 78	Water-soluble alkyd resin Water-soluble melamine resin	819
Comparative Example 58	Comp. Ex. 2	Water-soluble alkyd resin Water-soluble melamine resin	870
Comparative Example 59	Comp. Ex. 3	Water-soluble alkyd resin Water-soluble melamine resin	1,152
Comparative Example 60	Comp. Ex. 4	Water-soluble alkyd resin Water-soluble melamine resin	3,584

Table 16 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 93	96	16.6	7.8	0.8
Example 94	98	17.4	8.3	0.8
Example 95	96	17.3	7.9	0.8
Example 96	101	17.8	6.8	0.8
Example 97	106	18.2	7.9	0.7
Example 98	98	17.8	8.7	0.8
Example 99	90	17.8	9.6	0.9
Example 100	101	17.6	3.9	0.2
Example 101	106	17.8	3.8	0.2
Example 102	110	17.0	3.8	0.3
Example 103	113	16.9	3.1	0.3
Example 104	110	18.3	3.6	0.2
Example 105	96	17.6	4.8	0.3
Example 106	99	18.1	4.6	0.4
Comparative Example 58	60	23.1	13.1	2.0
Comparative Example 59	53	21.5	13.5	1.5
Comparative Example 60	46	20.7	14.6	1.7

Table 17

Examples and Comparative Examples	Production of resin composition	
	Black iron-based particles	
	Kinds	Amount (part by weight)
Example 107	Example 65	5.0
Example 108	Example 66	5.0
Example 109	Example 67	5.0
Example 110	Example 68	5.0
Example 111	Example 69	5.0
Example 112	Example 70	5.0
Example 113	Example 71	5.0
Example 114	Example 72	5.0
Example 115	Example 73	5.0
Example 116	Example 74	5.0
Example 117	Example 75	5.0
Example 118	Example 76	5.0
Example 119	Example 77	5.0
Example 120	Example 78	5.0
Comparative Example 61	Comparative Example 2	5.0
Comparative Example 62	Comparative Example 3	5.0
Comparative Example 63	Comparative Example 4	5.0

Table 17 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Example 107	Polyvinyl chloride resin	95.0
Example 108	Polyvinyl chloride resin	95.0
Example 109	Polyvinyl chloride resin	95.0
Example 110	Polyvinyl chloride resin	95.0
Example 111	Polyvinyl chloride resin	95.0
Example 112	Polyvinyl chloride resin	95.0
Example 113	Polyvinyl chloride resin	95.0
Example 114	Polyvinyl chloride resin	95.0
Example 115	Polyvinyl chloride resin	95.0
Example 116	Polyvinyl chloride resin	95.0
Example 117	Polyvinyl chloride resin	95.0
Example 118	Polyvinyl chloride resin	95.0
Example 119	Polyvinyl chloride resin	95.0
Example 120	Polyvinyl chloride resin	95.0
Comparative Example 61	Polyvinyl chloride resin	95.0
Comparative Example 62	Polyvinyl chloride resin	95.0
Comparative Example 63	Polyvinyl chloride resin	95.0

Table 17 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Example 107	Calcium stearate	1.0	160
Example 108	Calcium stearate	1.0	160
Example 109	Calcium stearate	1.0	160
Example 110	Calcium stearate	1.0	160
Example 111	Calcium stearate	1.0	160
Example 112	Calcium stearate	1.0	160
Example 113	Calcium stearate	1.0	160
Example 114	Calcium stearate	1.0	160
Example 115	Calcium stearate	1.0	160
Example 116	Calcium stearate	1.0	160
Example 117	Calcium stearate	1.0	160
Example 118	Calcium stearate	1.0	160
Example 119	Calcium stearate	1.0	160
Example 120	Calcium stearate	1.0	160
Comparative Example 61	Calcium stearate	1.0	160
Comparative Example 62	Calcium stearate	1.0	160
Comparative Example 63	Calcium stearate	1.0	160

Table 17 (continued)

Examples and Comparative Examples	Properties of resin composition				
	Dispers- ing condition  (-)	Blackness (L* value)  (-)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S <sub>0</sub> ) x 100 (%)		
			30 minutes	60 minutes	90 minutes
Example 107	5	17.6	0	5	5
Example 108	5	18.8	0	5	10
Example 109	5	18.8	0	0	5
Example 110	5	18.7	0	0	5
Example 111	5	19.6	0	5	5
Example 112	5	19.0	0	5	5
Example 113	4	19.3	0	5	10
Example 114	5	18.3	0	0	5
Example 115	5	18.6	0	0	0
Example 116	5	17.8	0	0	0
Example 117	5	18.1	0	0	0
Example 118	5	18.8	0	0	5
Example 119	5	18.5	0	5	5
Example 120	4	18.3	0	5	10
Comparative Example 61	3	24.5	10	20	25
Comparative Example 62	3	22.6	10	25	30
Comparative Example 63	3	21.8	15	25	35

Table 18

Examples and Comparative Examples	Kinds of core particles	Production of black iron- based composite particles or black iron-based particles	
		Addition of modified polysiloxane	
		Additives	
		Kinds	Amount added (part by weight)
Example 125	Core particles 1	BYK-080	1.0
Example 126	Core particles 2	BYK-080	0.5
Example 127	Core particles 3	BYK-310	2.0
Example 128	Core particles 4	BYK-322	5.0
Example 129	Core particles 5	TSF4446	1.0
Example 130	Core particles 6	TSF4460	3.0
Example 131	Core particles 7	YF3965	1.0
Example 132	Core particles 8	BYK-080	2.0
Example 133	Core particles 9	BYK-080	3.0
Example 134	Core particles 10	BYK-310	1.5
Example 135	Core particles 11	BYK-322	7.0
Example 136	Core particles 12	TSF4446	0.5
Example 137	Core particles 13	TSF4460	1.0
Example 138	Core particles 14	YF3965	2.5
Comparative Example 64	Core particles 1	BYK-080	1.0
Comparative Example 65	Core particles 3	BYK-080	0.5
Comparative Example 66	Core particles 3	BYK-080	0.005

Table 18 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of modified polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 125	60	30	0.18
Example 126	60	20	0.08
Example 127	60	20	0.35
Example 128	60	30	0.88
Example 129	60	30	0.17
Example 130	30	60	0.51
Example 131	60	15	0.15
Example 132	75	15	0.36
Example 133	60	20	0.50
Example 134	60	30	0.25
Example 135	45	45	1.21
Example 136	30	60	0.12
Example 137	30	30	0.18
Example 138	60	30	0.36
Comparative Example 64	60	30	0.16
Comparative Example 65	60	30	0.08
Comparative Example 66	60	30	$9.0 \times 10^{-4}$



Table 18 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles	
	Addition of carbon black fine particles	
	Carbon black fine particles	
	Kinds	Amount added (part by weight)
Example 125	A	8.0
Example 126	A	6.0
Example 127	A	6.5
Example 128	B	11.5
Example 129	B	15.0
Example 130	C	15.0
Example 131	C	10.0
Example 132	A	7.5
Example 133	A	12.5
Example 134	A	18.0
Example 135	B	15.0
Example 136	B	9.0
Example 137	C	17.0
Example 138	C	18.0
Comparative Example 64	-	-
Comparative Example 65	A	0.01
Comparative Example 66	B	5.0

Table 18 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or carbon black iron-based particles		
	Addition of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 125	30	30	7.41
Example 126	30	30	5.67
Example 127	60	60	6.09
Example 128	60	60	10.26
Example 129	30	45	12.91
Example 130	30	45	12.68
Example 131	60	30	9.06
Example 132	60	30	6.96
Example 133	45	45	11.07
Example 134	60	60	15.18
Example 135	30	50	13.11
Example 136	60	45	8.26
Example 137	45	60	14.55
Example 138	60	30	15.68
Comparative Example 64	-	-	-
Comparative Example 65	60	30	0.01
Comparative Example 66	60	30	4.76

Table 19

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Example 125	0.32	-	-	1.46
Example 126	0.18	-	-	1.40
Example 127	0.28	-	-	1.52
Example 128	0.23	-	-	1.34
Example 129	0.41	0.053	7.8	1.51
Example 130	0.28	0.038	7.3	1.39
Example 131	0.21	0.031	6.7	1.41
Example 132	0.32	-	-	1.44
Example 133	0.18	-	-	1.38
Example 134	0.29	-	-	1.47
Example 135	0.23	-	-	1.34
Example 136	0.40	0.051	7.8	1.50
Example 137	0.28	0.038	7.3	1.38
Example 138	0.19	0.028	6.7	1.42
Comparative Example 64	0.32	-	-	1.47
Comparative Example 65	0.28	-	-	1.52
Comparative Example 66	0.28	-	-	1.52

Table 19 (continued)

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	BET specific surface area (m <sup>2</sup> /g)	Mn content (wt. %)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 125	5.1	12.0	16.3	6.1
Example 126	7.6	14.6	17.8	8.3
Example 127	5.0	-	17.0	9.6
Example 128	13.6	-	16.4	9.2
Example 129	23.8	-	17.8	8.1
Example 130	91.6	14.6	17.8	7.6
Example 131	47.6	11.9	17.6	5.6
Example 132	4.6	11.6	16.5	4.1
Example 133	9.1	13.0	16.8	3.6
Example 134	14.4	-	15.9	2.8
Example 135	16.1	-	16.2	1.6
Example 136	24.8	-	17.5	4.6
Example 137	86.4	14.4	17.2	1.5
Example 138	48.1	11.5	17.3	1.8
Comparative Example 64	4.6	13.1	23.1	-
Comparative Example 65	5.6	-	21.4	-
Comparative Example 66	17.6	-	20.1	38.8

Table 20

Examples and Comparative Examples	Production of solvent-based paint		Properties of paint
	Kind of black iron- based particles	Kind of resin	Viscosity (cP)
Example 139	Example 125	Aminoalkyd resin	666
Example 140	Example 126	Aminoalkyd resin	794
Example 141	Example 127	Aminoalkyd resin	717
Example 142	Example 128	Aminoalkyd resin	614
Example 143	Example 129	Aminoalkyd resin	923
Example 144	Example 130	Aminoalkyd resin	845
Example 145	Example 131	Aminoalkyd resin	666
Example 146	Example 132	Aminoalkyd resin	717
Example 147	Example 133	Aminoalkyd resin	845
Example 148	Example 134	Aminoalkyd resin	768
Example 149	Example 135	Aminoalkyd resin	768
Example 150	Example 136	Aminoalkyd resin	666
Example 151	Example 137	Aminoalkyd resin	717
Example 152	Example 138	Aminoalkyd resin	640
Comparative Example 67	Comparative Example 64	Aminoalkyd resin	640
Comparative Example 68	Comparative Example 65	Aminoalkyd resin	921
Comparative Example 69	Comparative Example 66	Aminoalkyd resin	3,738

Table 20 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 139	105	15.8	7.8	0.7
Example 140	109	16.9	8.3	0.8
Example 141	98	16.7	7.6	0.7
Example 142	104	16.3	8.2	0.8
Example 143	90	17.8	8.9	0.8
Example 144	118	17.6	8.1	0.8
Example 145	122	17.6	7.4	0.7
Example 146	108	17.0	3.2	0.3
Example 147	115	16.6	3.8	0.2
Example 148	108	16.1	4.6	0.2
Example 149	106	16.5	2.3	0.3
Example 150	93	16.9	3.1	0.3
Example 151	127	17.3	3.9	0.4
Example 152	126	17.5	4.0	0.3
Comparative Example 67	76	22.2	11.2	1.7
Comparative Example 68	76	21.5	11.6	1.8
Comparative Example 69	43	19.9	13.6	1.4

Table 21

Examples and Comparative Examples	Production of water-based paint		Properties of paint
	Kinds of black iron-based particles	Kinds of resin	Viscosity (cP)
Example 153	Example 125	Water-soluble alkyd resin Water-soluble melamine resin	974
Example 154	Example 126	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 155	Example 127	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 156	Example 128	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 157	Example 129	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 158	Example 130	Water-soluble alkyd resin Water-soluble melamine resin	819
Example 159	Example 131	Water-soluble alkyd resin Water-soluble melamine resin	845
Example 160	Example 132	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 161	Example 133	Water-soluble alkyd resin Water-soluble melamine resin	640
Example 162	Example 134	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 163	Example 135	Water-soluble alkyd resin Water-soluble melamine resin	768
Example 164	Example 136	Water-soluble alkyd resin Water-soluble melamine resin	793
Example 165	Example 137	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 166	Example 138	Water-soluble alkyd resin Water-soluble melamine resin	870
Comparative Example 70	Comp. Ex. 64	Water-soluble alkyd resin Water-soluble melamine resin	742
Comparative Example 71	Comp. Ex. 65	Water-soluble alkyd resin Water-soluble melamine resin	1,254
Comparative Example 72	Comp. Ex. 66	Water-soluble alkyd resin Water-soluble melamine resin	3,712

Table 21 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 153	93	16.9	8.6	0.8
Example 154	97	17.6	8.6	0.8
Example 155	93	17.3	7.6	0.8
Example 156	96	17.8	7.8	0.8
Example 157	88	18.3	8.0	0.7
Example 158	112	17.9	7.6	0.7
Example 159	110	17.8	7.9	0.7
Example 160	101	17.7	4.3	0.4
Example 161	96	17.0	3.8	0.3
Example 162	98	17.1	3.2	0.2
Example 163	97	16.9	3.1	0.2
Example 164	91	18.2	4.4	0.3
Example 165	116	17.3	3.8	0.3
Example 166	112	17.8	4.1	0.4
Comparative Example 70	64	23.6	14.6	1.9
Comparative Example 71	60	21.8	14.8	1.9
Comparative Example 72	35	21.0	15.2	1.8



Table 22

Examples and Comparative Examples	Production of resin composition	
	Black iron-based particles	
	Kinds	Amount (part by weight)
Example 167	Example 125	5.0
Example 168	Example 126	5.0
Example 169	Example 127	5.0
Example 170	Example 128	5.0
Example 171	Example 129	5.0
Example 172	Example 130	5.0
Example 173	Example 131	5.0
Example 174	Example 132	5.0
Example 175	Example 133	5.0
Example 176	Example 134	5.0
Example 177	Example 135	5.0
Example 178	Example 136	5.0
Example 179	Example 137	5.0
Example 180	Example 138	5.0
Comparative Example 73	Comparative Example 64	5.0
Comparative Example 74	Comparative Example 65	5.0
Comparative Example 75	Comparative Example 66	5.0

Table 22 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Example 167	Polyvinyl chloride resin	95.0
Example 168	Polyvinyl chloride resin	95.0
Example 169	Polyvinyl chloride resin	95.0
Example 170	Polyvinyl chloride resin	95.0
Example 171	Polyvinyl chloride resin	95.0
Example 172	Polyvinyl chloride resin	95.0
Example 173	Polyvinyl chloride resin	95.0
Example 174	Polyvinyl chloride resin	95.0
Example 175	Polyvinyl chloride resin	95.0
Example 176	Polyvinyl chloride resin	95.0
Example 177	Polyvinyl chloride resin	95.0
Example 178	Polyvinyl chloride resin	95.0
Example 179	Polyvinyl chloride resin	95.0
Example 180	Polyvinyl chloride resin	95.0
Comparative Example 73	Polyvinyl chloride resin	95.0
Comparative Example 74	Polyvinyl chloride resin	95.0
Comparative Example 75	Polyvinyl chloride resin	95.0

Table 22 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Example 167	Calcium stearate	1.0	160
Example 168	Calcium stearate	1.0	160
Example 169	Calcium stearate	1.0	160
Example 170	Calcium stearate	1.0	160
Example 171	Calcium stearate	1.0	160
Example 172	Calcium stearate	1.0	160
Example 173	Calcium stearate	1.0	160
Example 174	Calcium stearate	1.0	160
Example 175	Calcium stearate	1.0	160
Example 176	Calcium stearate	1.0	160
Example 177	Calcium stearate	1.0	160
Example 178	Calcium stearate	1.0	160
Example 179	Calcium stearate	1.0	160
Example 180	Calcium stearate	1.0	160
Comparative Example 73	Calcium stearate	1.0	160
Comparative Example 74	Calcium stearate	1.0	160
Comparative Example 75	Calcium stearate	1.0	160

Table 22 (continued)

Examples and Comparative Examples	Properties of resin composition				
	Dispers- ing condition  (-)	Blackness (L* value)  (-)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S0) x 100 (%)		
			30 minutes	60 minutes	90 minutes
Example 167	5	17.7	0	5	5
Example 168	4	18.6	0	5	10
Example 169	5	18.6	0	0	5
Example 170	5	18.9	0	0	5
Example 171	4	19.4	0	5	5
Example 172	4	18.9	0	0	5
Example 173	5	18.8	0	0	5
Example 174	5	18.5	0	0	5
Example 175	5	18.1	0	0	0
Example 176	5	17.4	0	0	0
Example 177	5	17.8	0	0	0
Example 178	5	18.3	0	0	0
Example 179	5	18.4	0	0	0
Example 180	5	18.4	0	0	0
Comparative Example 73	3	24.5	10	15	25
Comparative Example 74	2	22.9	10	20	30
Comparative Example 75	3	21.8	15	25	35

Table 23

Examples and Comparative Examples	Kinds of core particles	Production of black iron- based composite particles or black iron-based particles	
		Addition of terminal- modified polysiloxane	
		Additives	
		Kinds	Amount added (part by weight)
Example 185	Core particles 1	TSF4770	2.0
Example 186	Core particles 2	TSF4770	1.0
Example 187	Core particles 3	TSF4751	0.5
Example 188	Core particles 4	TSF4751	3.0
Example 189	Core particles 5	XF-3905	5.0
Example 190	Core particles 6	XF-3905	1.5
Example 191	Core particles 7	YF-3804	2.0
Example 192	Core particles 8	TSF4770	1.0
Example 193	Core particles 9	TSF4770	3.0
Example 194	Core particles 10	TSF4751	0.5
Example 195	Core particles 11	TSF4751	1.7
Example 196	Core particles 12	XF-3905	2.0
Example 197	Core particles 13	XF-3905	1.0
Example 198	Core particles 14	YF-3804	1.5
Comparative Example 76	Core particles 1	TSF4770	1.0
Comparative Example 77	Core particles 3	TSF4770	1.0
Comparative Example 78	Core particles 3	TSF4770	0.005

Table 23 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of terminal-modified polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 185	60	30	0.45
Example 186	30	20	0.22
Example 187	60	20	0.12
Example 188	30	30	0.71
Example 189	45	30	1.11
Example 190	30	45	0.32
Example 191	45	60	0.44
Example 192	30	45	0.21
Example 193	30	20	0.68
Example 194	60	30	0.14
Example 195	30	45	0.38
Example 196	75	30	0.46
Example 197	60	45	0.21
Example 198	45	60	0.37
Comparative Example 76	30	30	0.26
Comparative Example 77	60	20	0.25
Comparative Example 78	45	30	$1.3 \times 10^{-3}$

Table 23 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles	
	Addition of carbon black fine particles	
	Carbon black fine particles	
	Kinds	Amount added (part by weight)
Example 185	A	10.0
Example 186	A	6.0
Example 187	A	8.0
Example 188	B	10.0
Example 189	B	15.0
Example 190	C	17.0
Example 191	C	10.0
Example 192	A	7.5
Example 193	A	12.0
Example 194	A	19.0
Example 195	B	13.0
Example 196	B	9.0
Example 197	C	16.0
Example 198	C	15.0
Comparative Example 76	-	-
Comparative Example 77	A	0.01
Comparative Example 78	B	5.0

Table 23 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of carbon black fine particles		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 185	60	30	9.12
Example 186	30	30	5.56
Example 187	45	45	7.43
Example 188	30	30	9.09
Example 189	60	60	12.96
Example 190	30	45	14.42
Example 191	30	60	9.10
Example 192	45	45	6.97
Example 193	60	45	10.73
Example 194	30	60	15.12
Example 195	45	30	11.46
Example 196	60	25	8.27
Example 197	45	20	13.60
Example 198	60	30	12.93
Comparative Example 76	-	-	-
Comparative Example 77	30	60	0.01
Comparative Example 78	60	45	4.73



Table 24

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Example 185	0.32	-	-	1.47
Example 186	0.18	-	-	1.40
Example 187	0.28	-	-	1.52
Example 188	0.23	-	-	1.35
Example 189	0.41	0.053	7.8	1.51
Example 190	0.28	0.038	7.3	1.39
Example 191	0.20	0.030	6.7	1.40
Example 192	0.32	-	-	1.44
Example 193	0.18	-	-	1.39
Example 194	0.29	-	-	1.49
Example 195	0.24	-	-	1.34
Example 196	0.40	0.051	7.8	1.49
Example 197	0.28	0.038	7.3	1.38
Example 198	0.19	0.028	6.7	1.41
Comparative Example 76	0.33	-	-	1.48
Comparative Example 77	0.28	-	-	1.52
Comparative Example 78	0.28	-	-	1.52

Table 24 (continued)

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	BET specific surface area (m <sup>2</sup> /g)	Mn content (wt. %)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 185	5.8	12.0	16.4	8.6
Example 186	7.8	14.8	18.0	7.9
Example 187	5.8	-	17.1	6.8
Example 188	14.1	-	16.6	8.1
Example 189	23.4	-	17.8	9.2
Example 190	93.8	15.1	17.9	8.6
Example 191	48.6	12.1	17.8	7.6
Example 192	5.1	11.8	16.6	3.6
Example 193	8.9	13.6	17.1	2.8
Example 194	13.8	-	16.4	3.2
Example 195	17.2	-	16.3	1.8
Example 196	26.8	-	17.8	0.9
Example 197	90.6	15.4	17.4	3.6
Example 198	47.8	11.8	17.5	4.1
Comparative Example 76	4.7	13.6	23.2	-
Comparative Example 77	6.6	-	21.5	-
Comparative Example 78	18.1	-	20.2	39.6

Table 25

Examples and Comparative Examples	Production of solvent-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 199	Example 185	Aminoalkyd resin	717
Example 200	Example 186	Aminoalkyd resin	870
Example 201	Example 187	Aminoalkyd resin	666
Example 202	Example 188	Aminoalkyd resin	538
Example 203	Example 189	Aminoalkyd resin	845
Example 204	Example 190	Aminoalkyd resin	923
Example 205	Example 191	Aminoalkyd resin	666
Example 206	Example 192	Aminoalkyd resin	589
Example 207	Example 193	Aminoalkyd resin	742
Example 208	Example 194	Aminoalkyd resin	845
Example 209	Example 195	Aminoalkyd resin	640
Example 210	Example 196	Aminoalkyd resin	717
Example 211	Example 197	Aminoalkyd resin	870
Example 212	Example 198	Aminoalkyd resin	896
Comparative Example 79	Comparative Example 76	Aminoalkyd resin	512
Comparative Example 80	Comparative Example 77	Aminoalkyd resin	840
Comparative Example 81	Comparative Example 78	Aminoalkyd resin	2,944

Table 25 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 199	100	15.7	7.3	0.8
Example 200	105	16.8	8.6	0.7
Example 201	98	16.6	7.1	0.8
Example 202	101	16.3	6.9	0.6
Example 203	91	17.8	8.1	0.8
Example 204	109	17.7	7.6	0.7
Example 205	113	17.7	7.1	0.7
Example 206	109	16.8	4.1	0.3
Example 207	108	16.8	3.6	0.3
Example 208	101	15.8	3.1	0.2
Example 209	106	16.4	2.8	0.2
Example 210	96	17.3	3.6	0.3
Example 211	131	17.1	1.3	0.3
Example 212	130	17.2	4.1	0.3
Comparative Example 79	78	22.1	11.1	1.5
Comparative Example 80	70	20.6	11.4	1.4
Comparative Example 81	43	19.4	12.8	1.3

Table 26

Examples and Comparative Examples	Production of water-based paint		Properties of paint
	Kind of black iron- based particles	Kind of resin	Viscosity (cP)
Example 213	Example 185	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 214	Example 186	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 215	Example 187	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 216	Example 188	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 217	Example 189	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 218	Example 190	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 219	Example 191	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 220	Example 192	Water-soluble alkyd resin Water-soluble melamine resin	819
Example 221	Example 193	Water-soluble alkyd resin Water-soluble melamine resin	768
Example 222	Example 194	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 223	Example 195	Water-soluble alkyd resin Water-soluble melamine resin	666
Example 224	Example 196	Water-soluble alkyd resin Water-soluble melamine resin	819
Example 225	Example 197	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 226	Example 198	Water-soluble alkyd resin Water-soluble melamine resin	845
Comparative Example 82	Comp. Ex. 76	Water-soluble alkyd resin Water-soluble melamine resin	717
Comparative Example 83	Comp. Ex. 77	Water-soluble alkyd resin Water-soluble melamine resin	896
Comparative Example 84	Comp. Ex. 78	Water-soluble alkyd resin Water-soluble melamine resin	3,584

Table 26 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 213	93	16.8	8.4	0.6
Example 214	96	17.7	7.8	0.7
Example 215	93	17.2	8.0	0.7
Example 216	98	17.6	6.8	0.8
Example 217	90	18.3	8.4	0.6
Example 218	106	17.6	8.1	0.7
Example 219	110	17.6	7.4	0.7
Example 220	100	17.8	3.8	0.3
Example 221	103	17.8	4.6	0.3
Example 222	101	17.8	4.1	0.4
Example 223	98	16.9	3.8	0.3
Example 224	96	18.5	3.2	0.2
Example 225	116	17.4	3.9	0.2
Example 226	113	17.8	3.6	0.3
Comparative Example 82	64	23.2	12.7	2.1
Comparative Example 83	60	21.6	13.6	2.1
Comparative Example 84	44	20.9	14.6	1.9

Table 27

Examples and Comparative Examples	Production of resin composition	
	Black iron-based particles	
	Kinds	Amount (part by weight)
Example 227	Example 185	5.0
Example 228	Example 186	5.0
Example 229	Example 187	5.0
Example 230	Example 188	5.0
Example 231	Example 189	5.0
Example 232	Example 190	5.0
Example 233	Example 191	5.0
Example 234	Example 192	5.0
Example 235	Example 193	5.0
Example 236	Example 194	5.0
Example 237	Example 195	5.0
Example 238	Example 196	5.0
Example 239	Example 197	5.0
Example 240	Example 198	5.0
Comparative Example 85	Comparative Example 76	5.0
Comparative Example 86	Comparative Example 77	5.0
Comparative Example 87	Comparative Example 78	5.0

Table 27 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Example 227	Polyvinyl chloride resin	95.0
Example 228	Polyvinyl chloride resin	95.0
Example 229	Polyvinyl chloride resin	95.0
Example 230	Polyvinyl chloride resin	95.0
Example 231	Polyvinyl chloride resin	95.0
Example 232	Polyvinyl chloride resin	95.0
Example 233	Polyvinyl chloride resin	95.0
Example 234	Polyvinyl chloride resin	95.0
Example 235	Polyvinyl chloride resin	95.0
Example 236	Polyvinyl chloride resin	95.0
Example 237	Polyvinyl chloride resin	95.0
Example 238	Polyvinyl chloride resin	95.0
Example 239	Polyvinyl chloride resin	95.0
Example 240	Polyvinyl chloride resin	95.0
Comparative Example 85	Polyvinyl chloride resin	95.0
Comparative Example 86	Polyvinyl chloride resin	95.0
Comparative Example 87	Polyvinyl chloride resin	95.0



Table 27 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Example 227	Calcium stearate	1.0	160
Example 228	Calcium stearate	1.0	160
Example 229	Calcium stearate	1.0	160
Example 230	Calcium stearate	1.0	160
Example 231	Calcium stearate	1.0	160
Example 232	Calcium stearate	1.0	160
Example 233	Calcium stearate	1.0	160
Example 234	Calcium stearate	1.0	160
Example 235	Calcium stearate	1.0	160
Example 236	Calcium stearate	1.0	160
Example 237	Calcium stearate	1.0	160
Example 238	Calcium stearate	1.0	160
Example 239	Calcium stearate	1.0	160
Example 240	Calcium stearate	1.0	160
Comparative Example 85	Calcium stearate	1.0	160
Comparative Example 86	Calcium stearate	1.0	160
Comparative Example 87	Calcium stearate	1.0	160

Table 27 (continued)

Examples and Comparative Examples	Properties of resin composition				
	Dispers- ing condition  (-)	Blacknes s (L* value)  (-)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S0) x 100 (%)		
			30 minutes	60 minutes	90 minutes
Example 227	4	17.6	0	5	5
Example 228	4	18.8	0	5	10
Example 229	5	18.6	0	5	5
Example 230	5	18.7	0	0	5
Example 231	4	19.7	0	5	10
Example 232	4	18.8	0	5	10
Example 233	4	18.7	0	5	5
Example 234	5	18.5	0	0	0
Example 235	5	18.6	0	0	0
Example 236	5	17.2	0	0	5
Example 237	5	18.3	0	0	5
Example 238	5	18.2	0	0	0
Example 239	5	18.3	0	5	5
Example 240	5	18.1	0	0	0
Comparative Example 85	3	24.4	10	15	20
Comparative Example 86	3	22.9	10	20	30
Comparative Example 87	3	21.8	10	25	35

Table 28

Examples and Comparative Examples	Kind of core particles	Production of black iron- based composite particles or black iron-based particles	
		Addition of fluoroalkylsilane	
		Additives	
		Kinds	Amount added (part by weight)
Example 245	Core particles 1	TSL-8257	2.0
Example 246	Core particles 2	TSL-8233	4.0
Example 247	Core particles 3	TSL-8262	3.0
Example 248	Core particles 4	TSL-8257	1.0
Example 249	Core particles 5	TSL-8233	10.0
Example 250	Core particles 6	TSL-8262	2.0
Example 251	Core particles 7	TSL-8257	3.0
Example 252	Core particles 8	TSL-8257	6.0
Example 253	Core particles 9	TSL-8233	4.0
Example 254	Core particles 10	TSL-8262	0.5
Example 255	Core particles 11	TSL-8257	1.5
Example 256	Core particles 12	TSL-8233	2.0
Example 257	Core particles 13	TSL-8262	0.8
Example 258	Core particles 14	TSL-8257	4.0
Comparative Example 88	Core particles 1	TSL-8257	2.0
Comparative Example 89	Core particles 3	TSL-8257	30
Comparative Example 90	Core particles 3	TSL-8257	0.005

Table 28 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of fluoroalkylsilane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 245	60	30	0.13
Example 246	60	30	0.21
Example 247	60	15	0.48
Example 248	60	20	0.07
Example 249	60	60	0.54
Example 250	30	30	0.32
Example 251	60	60	0.20
Example 252	75	30	0.40
Example 253	60	15	0.21
Example 254	60	20	0.08
Example 255	45	60	0.10
Example 256	30	30	0.11
Example 257	30	30	0.13
Example 258	60	30	0.26
Comparative Example 88	60	20	0.13
Comparative Example 89	60	30	0.2
Comparative Example 90	60	30	$3.3 \times 10^{-4}$

Table 28 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles	
	Addition of carbon black fine particles	
	Carbon black fine particles	
	Kinds	Amount added (part by weight)
Example 245	A	8.0
Example 246	A	6.0
Example 247	A	5.0
Example 248	B	13.0
Example 249	B	18.0
Example 250	C	15.0
Example 251	C	15.0
Example 252	A	10.0
Example 253	A	10.0
Example 254	A	18.0
Example 255	B	16.0
Example 256	B	9.0
Example 257	C	16.0
Example 258	C	15.0
Comparative Example 88	-	-
Comparative Example 89	A	0.01
Comparative Example 90	B	5.0

Table 28 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 245	30	60	7.42
Example 246	60	30	5.68
Example 247	45	30	4.78
Example 248	60	60	11.53
Example 249	45	75	15.16
Example 250	30	40	13.03
Example 251	45	45	13.04
Example 252	60	45	9.01
Example 253	60	60	9.09
Example 254	30	30	15.18
Example 255	30	20	13.81
Example 256	60	60	8.26
Example 257	30	20	13.76
Example 258	60	—	12.99
Comparative Example 88	-	-	-
Comparative Example 89	60	30	0.01
Comparative Example 90	60	30	4.76

Table 29

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Example 245	0.32	-	-	1.47
Example 246	0.18	-	-	1.41
Example 247	0.28	-	-	1.53
Example 248	0.23	-	-	1.35
Example 249	0.40	0.051	7.8	1.53
Example 250	0.28	0.038	7.3	1.38
Example 251	0.20	0.030	6.7	1.41
Example 252	0.32	-	-	1.48
Example 253	0.19	-	-	1.41
Example 254	0.29	-	-	1.52
Example 255	0.24	-	-	1.35
Example 256	0.41	0.053	7.8	1.53
Example 257	0.29	0.040	7.3	1.38
Example 258	0.20	0.030	6.7	1.41
Comparative Example 88	0.33	-	-	1.47
Comparative Example 89	0.32	-	-	1.48
Comparative Example 90	0.28	-	-	1.51

Table 29 (continued)

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	BET specific surface area (m <sup>2</sup> /g)	Mn content (wt. %)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 245	5.0	12.1	16.4	7.1
Example 246	7.4	14.7	18.0	8.6
Example 247	5.3	-	17.2	6.9
Example 248	13.0	-	16.6	5.8
Example 249	21.6	-	17.7	5.9
Example 250	89.7	14.5	17.9	6.9
Example 251	46.6	11.8	17.5	7.5
Example 252	4.8	11.5	16.6	3.6
Example 253	8.9	12.9	16.9	2.8
Example 254	13.8	-	15.8	0.6
Example 255	15.8	-	16.3	1.8
Example 256	23.6	-	17.3	3.2
Example 257	83.1	14.4	17.2	4.6
Example 258	47.1	11.5	17.2	4.8
Comparative Example 88	16.6	12.0	21.3	68.3
Comparative Example 89	4.7	13.1	23.0	-
Comparative Example 90	5.6	-	21.4	-



Table 30

Examples and Comparative Examples	Production of solvent-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 259	Example 245	Aminoalkyd resin	666
Example 260	Example 246	Aminoalkyd resin	793
Example 261	Example 247	Aminoalkyd resin	614
Example 262	Example 248	Aminoalkyd resin	666
Example 263	Example 249	Aminoalkyd resin	768
Example 264	Example 250	Aminoalkyd resin	845
Example 265	Example 251	Aminoalkyd resin	896
Example 266	Example 252	Aminoalkyd resin	614
Example 267	Example 253	Aminoalkyd resin	712
Example 268	Example 254	Aminoalkyd resin	712
Example 269	Example 255	Aminoalkyd resin	538
Example 270	Example 256	Aminoalkyd resin	640
Example 271	Example 257	Aminoalkyd resin	845
Example 272	Example 258	Aminoalkyd resin	712
Comparative Example 91	Comparative Example 88	Aminoalkyd resin	538
Comparative Example 92	Comparative Example 89	Aminoalkyd resin	845
Comparative Example 93	Comparative Example 90	Aminoalkyd resin	4,096

Table 30 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 259	105	15.9	7.8	0.7
Example 260	109	16.8	9.2	0.8
Example 261	98	16.5	8.6	0.9
Example 262	106	16.3	7.4	0.6
Example 263	93	17.3	7.3	0.6
Example 264	118	17.4	6.9	0.7
Example 265	122	17.1	8.1	0.8
Example 266	110	16.5	4.1	0.3
Example 267	111	16.6	4.6	0.3
Example 268	106	15.8	2.3	0.4
Example 269	103	15.9	1.8	0.3
Example 270	94	16.9	3.4	0.2
Example 271	128	17.2	3.2	0.4
Example 272	123	17.4	3.7	0.3
Comparative Example 91	81	22.1	11.3	1.7
Comparative Example 92	73	20.7	11.6	1.8
Comparative Example 93	48	19.8	12.5	1.6

Table 31

Examples and Comparative Examples	Production of water-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 273	Example 245	Water-soluble alkyd resin Water-soluble melamine resin	845
Example 274	Example 246	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 275	Example 247	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 276	Example 248	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 277	Example 249	Water-soluble alkyd resin Water-soluble melamine resin	922
Example 278	Example 250	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 279	Example 251	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 280	Example 252	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 281	Example 253	Water-soluble alkyd resin Water-soluble melamine resin	640
Example 282	Example 254	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 283	Example 255	Water-soluble alkyd resin Water-soluble melamine resin	768
Example 284	Example 256	Water-soluble alkyd resin Water-soluble melamine resin	845
Example 285	Example 257	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 286	Example 258	Water-soluble alkyd resin Water-soluble melamine resin	666
Comparative Example 94	Comp. Ex. 88	Water-soluble alkyd resin Water-soluble melamine resin	717
Comparative Example 95	Comp. Ex. 89	Water-soluble alkyd resin Water-soluble melamine resin	922
Comparative Example 96	Comp. Ex. 90	Water-soluble alkyd resin Water-soluble melamine resin	2,560

Table 31 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 273	92	16.6	8.6	0.7
Example 274	96	17.1	8.7	0.8
Example 275	93	17.4	8.2	0.7
Example 276	98	17.6	7.2	0.8
Example 277	90	18.3	8.3	0.7
Example 278	106	17.5	8.1	0.8
Example 279	111	17.3	7.8	0.9
Example 280	96	17.5	4.3	0.3
Example 281	99	17.3	4.0	0.3
Example 282	98	16.8	3.9	0.2
Example 283	97	17.3	2.1	0.2
Example 284	91	18.1	3.6	0.3
Example 285	113	17.5	2.8	0.4
Example 286	113	17.7	2.6	0.3
Comparative Example 94	66	23.6	14.1	2.5
Comparative Example 95	63	22.0	14.8	2.0
Comparative Example 96	46	21.0	14.6	1.9

Table 32

Examples and Comparative Examples	Production of resin composition	
	Black iron-based particles	
	Kinds	Amount (part by weight)
Example 287	Example 245	5.0
Example 288	Example 246	5.0
Example 289	Example 247	5.0
Example 290	Example 248	5.0
Example 291	Example 249	5.0
Example 292	Example 250	5.0
Example 293	Example 251	5.0
Example 294	Example 252	5.0
Example 295	Example 253	5.0
Example 296	Example 254	5.0
Example 297	Example 255	5.0
Example 298	Example 256	5.0
Example 299	Example 257	5.0
Example 300	Example 258	5.0
Comparative Example 97	Comparative Example 88	5.0
Comparative Example 98	Comparative Example 89	5.0
Comparative Example 99	Comparative Example 90	5.0

Table 32 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Example 287	Polyvinyl chloride resin	95.0
Example 288	Polyvinyl chloride resin	95.0
Example 289	Polyvinyl chloride resin	95.0
Example 290	Polyvinyl chloride resin	95.0
Example 291	Polyvinyl chloride resin	95.0
Example 292	Polyvinyl chloride resin	95.0
Example 293	Polyvinyl chloride resin	95.0
Example 294	Polyvinyl chloride resin	95.0
Example 295	Polyvinyl chloride resin	95.0
Example 296	Polyvinyl chloride resin	95.0
Example 297	Polyvinyl chloride resin	95.0
Example 298	Polyvinyl chloride resin	95.0
Example 299	Polyvinyl chloride resin	95.0
Example 300	Polyvinyl chloride resin	95.0
Comparative Example 97	Polyvinyl chloride resin	95.0
Comparative Example 98	Polyvinyl chloride resin	95.0
Comparative Example 99	Polyvinyl chloride resin	95.0

Table 32 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Example 287	Calcium stearate	1.0	160
Example 288	Calcium stearate	1.0	160
Example 289	Calcium stearate	1.0	160
Example 290	Calcium stearate	1.0	160
Example 291	Calcium stearate	1.0	160
Example 292	Calcium stearate	1.0	160
Example 293	Calcium stearate	1.0	160
Example 294	Calcium stearate	1.0	160
Example 295	Calcium stearate	1.0	160
Example 296	Calcium stearate	1.0	160
Example 297	Calcium stearate	1.0	160
Example 298	Calcium stearate	1.0	160
Example 299	Calcium stearate	1.0	160
Example 300	Calcium stearate	1.0	160
Comparative Example 97	Calcium stearate	1.0	160
Comparative Example 98	Calcium stearate	1.0	160
Comparative Example 99	Calcium stearate	1.0	160

Table 32 (continued)

Examples and Comparative Examples	Properties of resin composition				
	Dispersing condition (-)	Blackness (L* value) (-)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S0) x 100 (%)		
			30 minutes	60 minutes	90 minutes
Example 287	5	17.6	0	5	5
Example 288	5	18.6	0	5	10
Example 289	5	18.1	0	5	5
Example 290	4	18.8	0	0	5
Example 291	4	19.1	0	5	10
Example 292	4	18.6	0	5	10
Example 293	5	18.7	0	5	5
Example 294	5	18.3	0	0	5
Example 295	5	18.5	0	0	0
Example 296	5	17.5	0	0	5
Example 297	5	17.9	0	0	0
Example 298	5	18.4	0	0	0
Example 299	5	18.1	0	0	5
Example 300	5	18.2	0	0	0
Comparative Example 97	3	24.5	10	15	25
Comparative Example 98	3	22.9	15	20	30
Comparative Example 99	3	22.1	15	20	35

## Claims

1. Black iron-based composite particles comprising:



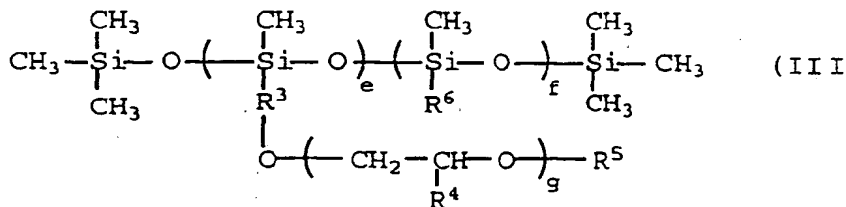
- (i) black iron oxide particles or black iron oxide hydroxide particles having an average particle size of 0.08 to 1.0  $\mu\text{m}$ ;  
 (ii) a coating layer on the surface of said particles, said coating layer comprising an organosilicon compound which is:

- (1) an organosilane compound obtainable by drying or heat-treating an alkoxysilane compound,  
 (2) a polysiloxane or modified polysiloxane, or  
 (3) a fluoroalkyl organosilane compound obtainable by drying or heat-treating a fluoroalkylsilane compound; and

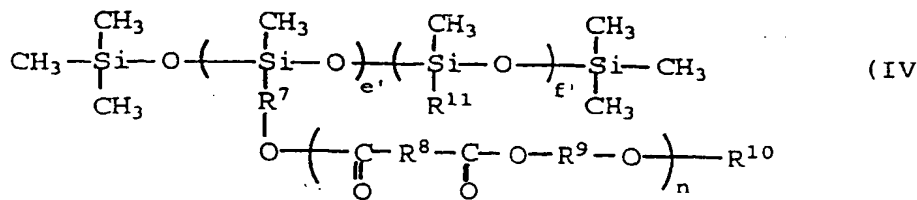
- (iii) carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$ , adhered on at least a part of said coating layer.

the amount of said carbon black fine particles adhered being 1 to 30 parts by weight based on 100 parts by weight of said particles (i).

2. Composite particles according to claim 1, which further comprise an underlayer formed between said particle (i) and said coating layer (ii), comprising a hydroxide of aluminum, oxide of aluminum, hydroxide of silicon or oxide of silicon.
3. Composite particles according to claim 2, wherein the amount of said hydroxide of aluminum or silicon, or oxide of aluminum or silicon is 0.01 to 50 % by weight, calculated as Al or  $\text{SiO}_2$ , based on the weight of said black iron oxide particles or black iron oxide hydroxide particles.
4. Composite particles according to any one of the preceding claims, wherein said modified polysiloxane is
- (A) a polysiloxane modified with a polyether, polyester or epoxy compound; or  
 (B) a polysiloxane whose molecular terminal is modified with a carboxylic acid group, alcohol group or a hydroxyl group.
5. Composite particles according to claim 4, wherein said polysiloxane (A) is of formula (III), (IV) or (V):

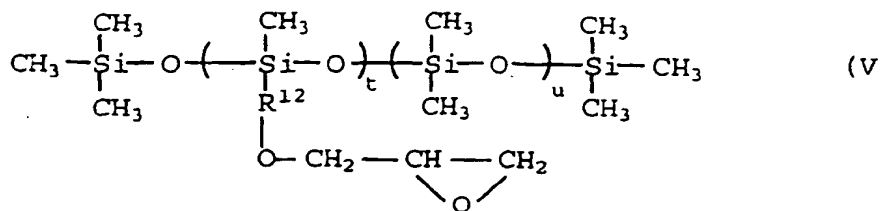


wherein  $\text{R}^3$  is  $-(\text{CH}_2)_h-$ ;  $\text{R}^4$  is  $-(\text{CH}_2)_i-\text{CH}_3$ ;  $\text{R}^5$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}(\text{CH}_3)=\text{CH}_2$  or  $-(\text{CH}_2)_j-\text{CH}_3$ ;  $\text{R}^6$  is  $-(\text{CH}_2)_k-\text{CH}_3$ ; g and h are each independently an integer of from 1 to 15; i, j and k are each independently an integer of from 0 to 15; e is an integer of from 1 to 50; and f is an integer of from 1 to 300;



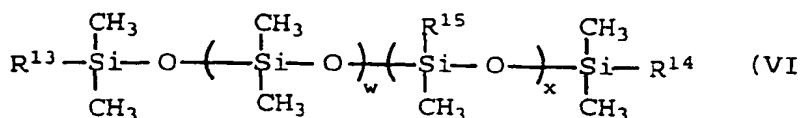
wherein  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  are each  $-(\text{CH}_2)_q-$  and may be the same or different;  $\text{R}^{10}$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}$

$(\text{CH}_3)_2\text{CH}_2$  or  $(-\text{CH}_2-)_r-\text{CH}_3$ ;  $\text{R}^{11}$  is  $(-\text{CH}_2-)_s-\text{CH}_3$ ;  $n$  and  $q$  are each independently an integer of from 1 to 15;  $r$  and  $s$  are each independently an integer of from 0 to 15;  $e'$  is an integer of from 1 to 50; and  $f'$  is an integer of from 1 to 300; or



wherein  $\text{R}^{12}$  is  $(-\text{CH}_2-)_v$ ;  $v$  is an integer of from 1 to 15;  $t$  is an integer of from 1 to 50; and  $u$  is an integer of from 1 to 300.

6. Composite particles according to claim 4 or 5, wherein said polysiloxane (B) is of formula (VI):



wherein  $\text{R}^{13}$  and  $\text{R}^{14}$  are each  $-\text{OH}$ ,  $\text{R}^{16}\text{OH}$  or  $\text{R}^{17}\text{COOH}$  and may be the same or different;  $\text{R}^{15}$  is  $-\text{CH}_3$  or  $-\text{C}_6\text{H}_5$ ;  $\text{R}^{16}$  and  $\text{R}^{17}$  are each independently  $(-\text{CH}_2-)_y$ ;  $y$  is an integer of from 1 to 15;  $w$  is an integer of from 1 to 200; and  $x$  is an integer of from 0 to 100.

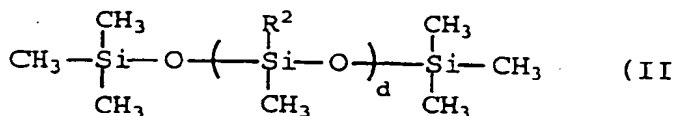
7. Composite particles according to any one of the preceding claims, wherein said alkoxy silane compound is of formula (I):



wherein  $\text{R}^1$  is  $\text{C}_6\text{H}_5-$ ,  $(\text{CH}_3)_2\text{CHCH}_2-$  or  $n\text{-C}_m\text{H}_{2m+1}-$  (wherein  $m$  is an integer of from 1 to 18);  $\text{X}$  is  $\text{CH}_3\text{O}-$  or  $\text{C}_2\text{H}_5\text{O}-$ ; and  $a$  is an integer of from 0 to 3.

8. Composite particles according to claim 7, wherein said alkoxy silane compound is methyl triethoxysilane, dimethyl diethoxysilane, tetraethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane, tetramethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, isobutyl trimethoxysilane or decyl trimethoxysilane.

9. Composite particles according to any one of the preceding claims wherein said polysiloxane is of formula (II):



wherein  $\text{R}^2$  is  $\text{H}-$  or  $\text{CH}_3-$ , and  $d$  is an integer of from 15 to 450.

10. Composite particles according to claim 9, wherein said polysiloxane has methyl hydrogen siloxane units.

11. Composite particles according to any one of the preceding claims, wherein said fluoroalkyl organosilane compound is of general formula (VII):



wherein  $\text{R}^{18}$  is  $\text{CH}_3$ -,  $\text{C}_2\text{H}_5$ -,  $\text{CH}_3\text{O}$ - or  $\text{C}_2\text{H}_5\text{O}$ -; X is  $\text{CH}_3\text{O}$ - or  $\text{C}_2\text{H}_5\text{O}$ -; and z is an integer of from 0 to 15; and a is an integer of from 0 to 3.

12. Composite particles according to any one of the preceding claims which have:

a blackness ( $L^*$  value) of 15 to 18, and/or  
a particle size of 0.082 to 1.05  $\mu\text{m}$ , and/or

a BET specific surface area value of 1 to 200  $\text{m}^2/\text{g}$ , and/or  
a geometrical standard deviation of particle sizes of 1.01 to 1.8.

13. Composite particles according to any one of the preceding claims wherein said particles (i) are magnetite particles, manganese-containing hematite particles or manganese-containing goethite particles.

14. Composite particles according to any one of the preceding claims, wherein the amount of said coating organosilicon compound (ii) is 0.02 to 5.0 % by weight, calculated as Si, based on the total weight of the organosilicon compound (ii) and said particles (i).

15. A process for producing black iron-based composite particles as claimed in any one of the preceding claims, which process comprises:

(a) mixing and stirring said particles (i) together with a silicon-containing compound which is:

- (1) an alkoxysilane compound,
- (2) a polysiloxane or modified polysiloxane, or
- (3) a fluoroalkylsilane compound using an edge runner, thereby coating the surface of said particles (i) with said compound;

(b) adding carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$  in an amount of 1 to 30 parts by weight based on 100 parts by weight of said particles (i), thereby obtaining mixed particles; and  
(c) mixing and stirring said mixed particles using an edge runner, followed by  
(d) drying or heat-treating, thereby adhering said carbon black fine particles on the surface of a coating layer comprising the organosilicon compound.

16. A process according to claim 15, wherein said particles (i) have been coated with a hydroxide of aluminum, oxide of aluminum, hydroxide of silicon or oxide of silicon.

17. A paint comprising:

said black iron-based composite particles as claimed in any one of claims 1 to 14 or as produced by a process according to claims 15 or 16; and  
a paint base material.

18. A paint according to claim 17, wherein the amount of said composite particles is 1.0 to 100 parts by weight based on 100 parts by weight of said paint base material.

19. A rubber or resin composition comprising:

said black iron-based composite particles as claimed in any one of claims 1 to 14 or as produced by a process according to claims 15 or 16; and  
a base material for a rubber or resin composition.

**EP 0 913 431 A2**

- 20.** A rubber or resin composition according to claim 19, wherein the amount of said composite particles is 0.5 to 200 parts by weight based on 100 parts by weight of said base material.

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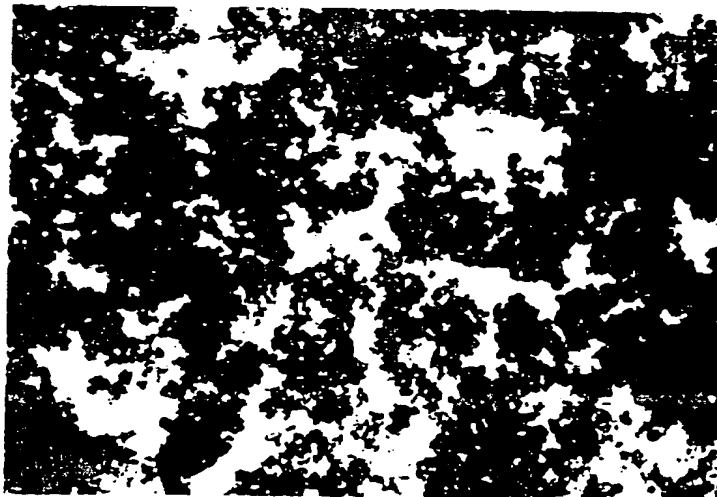
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**FIG.1**



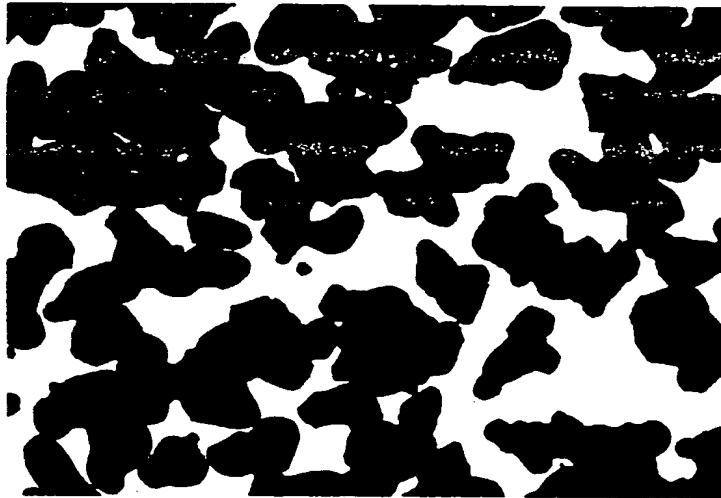
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**FIG.2**



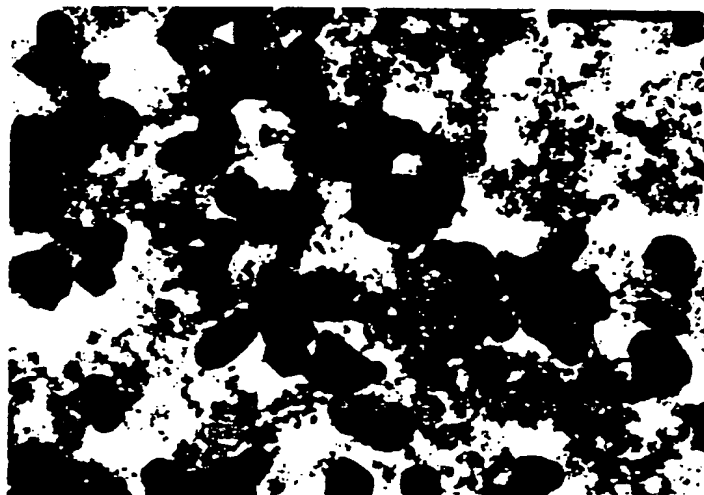
( $\times 20000$ )

**FIG.3**



( $\times 20000$ )

**FIG.4**



( $\times 20000$ )



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(54) **Black iron-based composite particles, process for producing the same, paint and rubber or resin composition containing the same**

(57) Black iron-based composite particles of the present invention comprise:

- (i) black iron oxide particles or black iron oxide hydroxide particles having an average particle size of 0.08 to 1.0  $\mu\text{m}$ ;
- (ii) a coating layer formed on the surface of said particles (i) said coating layer comprising an organosilicon compound which is:

- (1) an organosilane compound obtainable by drying or heat-treating an alkoxysilane compound,
- (2) a polysiloxane or modified polysiloxane, or

(3) a fluoroalkyl organosilane compound obtainable by drying or heat-treating a fluoroalkylsilane compound; and

(iii) carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$ , adhered on at least a part of said coating layer. Such composite particles have excellent dispersibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the composite particles. They also have a high blackness substantially identical to a blackness of carbon black fine particles used alone, even when carbon black is contained therein only in a small amount.

EP 0 913 431 A3



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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 8925

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.8)
A	FR 2 030 604 A (PFIZER) 13 November 1970 (1970-11-13) * page 4, line 15-28; claims 1-14; examples 2,3 *	1, 15, 17, 19	C09C1/24 C09D5/00
A	GB 1 178 050 A (PFIZER) 14 January 1970 (1970-01-14) * claims 1-21; examples 2,3 *	1, 15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.8)
			C09C C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 August 1999	Examiner Drouot, M-C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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ANNEX TO THE EUROPEAN SEARCH REPORT  
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EP 98 30 8925

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12-08-1999

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
FR 2030604	A	13-11-1970	NONE		
GB 1178050	A	14-01-1970	US	3619227 A	09-11-1971

EPO FORM P0459

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